An experimental and macromechanical study of two-way shape recovery characteristics in NiTi alloy

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**AN EXPERIMENTAL AND MACROMECHANICAL
STUDY OF TWO-WAY SHAPE RECOVERY
CHARACTERISTICS IN NITI ALLOY**

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**KIYOHIDE WADA
2008**

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SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING
2008**

**An Experimental and Macromechanical Study of
Two-way Shape Recovery Characteristics
in NiTi Alloy**

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Abstract

Thermomechanical treatment can greatly influence the shape recovery characteristics of Nickel Titanium (NiTi) alloy, such as recovery stress, strain and transformation temperatures. One aspect of this treatment is commonly known as “*training*” where the specimen is thermally cycled under constraint, resulting in the development of stress-assisted two-way memory effect (SATWME). Training is an important process to further develop a spontaneous recovery of hot and cold shapes known as two-way memory effect (TWME). Although extensive experimental and theoretical works have been carried out to date, interpretation of the mechanism giving rise to these memory effects is still unclear and a debatable subject.

The present research is dedicated to identify the predominant factors responsible for the development of SATWME and TWME. The characterization of the thermomechanical correlation of these memory effects is of particular interest.

The experimental results show that the SATWME and TWME are controlled predominantly by four factors: pre-strain, constrained stress, propagation of martensite deformation during thermal cycling and the nature of thermal cycling (full/partial reverse transformation). Increasing the pre-strain magnitude causes martensite detwinning and dislocation generation. Full utilization of martensite detwinning capacity, whether achieved by the direct application of pre-strain or by the cyclic shift of martensitic strain, results in the maximum SATWME and TWME. The magnitude of constrained stress is critical in determining the microstructural

Abstract

potency to align/realign the generated dislocation structures. Partial reverse transformation through thermal arrest during heating leads to the accommodation of stress-assisted and detwinned martensite variants. Such accommodation process causes the internal forward and back stress formations.

The effects of partial transformation on the SATWME and TWME are studied by the macromechanical approaches. A strain comparison approach demonstrates that the generation of two-step reverse transformation is proceeded by the sequential transformation of stress-assisted and detwinned martensite variants in the order of increasing temperature. SATWME under 350MPa cycling is dominated by the stress-assisted martensite. Consequently, from an equal strain position (ESP) analysis, it is demonstrated that internal back stress formation is promoted by this effect. TWME is promoted through dominant internal forward stress formation, while the dominance of internal back stress reduces the TWME by decreasing the martensitic strain.

A two-step transformation model is proposed on the basis of dislocation pile-up theory, strain comparison and ESP analysis.

Based on the thermodynamic analysis, the thermomechanical mechanisms involved in the development of SATWME and TWME, though similar at their maximum recovery strain magnitudes, they are different below and above the maximum level. It is also demonstrated that the appearance of two-step reverse transformation is a one-time only phenomenon.

The presented experimental and macromechanical results create a more in-depth knowledge towards understanding the principle mechanism of two-way shape recovery characteristics in NiTi and other alloy systems.

To my mentor, Ikeda Sensei

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Claims of Originality

A spontaneous reversible shape change between high and low temperatures is known as two-way memory effect (TWME) and can be realized through constrained thermal cycling. TWME requires no resetting bias force and therefore provides an ideal solution to various engineering applications. The subject of constrained recovery and its relation to TWME is essential for an understanding of many of the thermomechanical mechanisms operating behind the TWME.

Apart from generally accepted ideas, concepts and formulations or where specific reference is made to the works of other authors, the following original contributions are made in this thesis:

- Experimental results that clarify the development mechanism and the thermomechanical correlation of stress-assisted two-way memory effect (SATWME) and TWME.
- Experimental results that demonstrate the emergence and characteristic of two-step reverse transformation due to various thermomechanical conditions.
- A schematic model representing the development of internal forward and back stresses due to various thermomechanical conditions.
- A pre-positioning and overheating mechanism of two-step reverse transformation.

Claims of Originality

- A strain comparison and equal strain position analysis applied to interpret the accommodation process of distinctively oriented martensite variants.
- A two-step transformation model.

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A	Area/Austenite
A_f	Austenite finish temperature
A_p	Austenite peak temperature
A_s	Austenite start temperature
ΔA	Temperature interval of reverse transformation ($M \rightarrow A$)
b	Burgers vector
D	Defects
E_{el}	Elastic strain energy
E_{fr}	Irreversible frictional energy
F	Force
G	Total Gibbs free energy change
G_{ch}	Total Gibbs free energy change (chemical)
G_{nch}	Total Gibbs free energy change (non-chemical)
H	Transformation enthalpy
H_{ch}	Chemical transformation enthalpy
H_{net}	Net transformation enthalpy measured by calorimetry
M	Martensite
M_f	Martensite finish temperature

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M_p	Martensite peak temperature
M_s	Martensite start temperature
M	Temperature interval of forward transformation ($A \rightarrow M$)
P	Pressure
Q	Heat flow
R_p	R -phase peak temperature
S	Transformation entropy
T	Temperature
T_{eq}	Revised equilibrium temperature (when $\Delta G_{ch} + \Delta G_{nch} = 0$)
T_H	Target temperature (set between A_s and A_f temperatures)
T_k	Kinetic stop temperature
T_0	Equilibrium temperature (when $\Delta G_{ch} = 0$)
T_0'	Equilibrium temperature (when $\Delta G_{ch} + \Delta G_{nch} = 0$)
U	Internal energy
V	Volume of the specimen
W	Mechanical work done
ε	Engineering strain
ε_{FT}	Fully transformed strain
ε_{IR}	Irrecoverable strain
ε_{MA}	Martensitic strain
ε_{PT}	Partially transformed strain
ε_{RS}	Residual strain
ε_{RM}	Non-transformed strain (i.e. retained martensite)
ε_{SATW}	Stress-assisted two-way memory strain

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ε_{TR}	Transformation strain
ε_{TW}	Two-way memory strain
γ	Shear strain
ρ	Density
σ	Engineering tensile stress
σ_{INT}	Internal stress
σ_i^F	Internal forward stress
σ_i^B	Internal back stress
σ_y	First yield stress (at the onset of stress-plateau)
σ_y'	Second yield stress
τ	Shear stress
ν	Poisson's ratio

SUBSCRIPTS

c = at critical, cs = cross-slip, f = friction, m = mobile, N = at N^{th} cycle, 0 = at equilibrium, T_{eq} = at equilibrium temperature.

SUPERSCRIPTS

d = defects, s = supplemental, t = transformation, 1 = first-half of reverse transformation, 2 = second-half of reverse transformation.

CHAPTER 1

Introduction

The fascination of shape memory alloys (SMAs) is deeply rooted in their unique ability to recover from apparent deformed shape to its original undeformed shape. This ability is manifested either by releasing the applied load or upon heating. Thermally-induced shape recovery phenomenon, namely the shape memory effect (SME) was first discovered in a binary alloy of Gold-Cadmium [1, 2]. Since then, researchers have extended their interest to discover SME in other alloy systems. Of these alloy systems include Fe-based alloys [3, 4], Cu-based alloys [5-8], Ni-Ti alloys [9-11] and others [2, 12-15]. A near equiatomic NiTi alloy in particular is well known for its distinctive advantage in strength-to-weight ratios, fatigue resistance, damping capacity and excellence in bio-compatibility [16-19].

The working characteristics of SMA element, for the causes of shape recovery behavior, are mainly controlled by the thermomechanical treatment, e.g. combination of externally applied stress, strain and temperature. With the high complexity of shape recovery mechanisms that involves hysteretic and nonlinear response during phase transformation make it extremely difficult for the model-based simulation. Aspired by this challenge, much thorough research work is needed, providing new knowledge to strengthen our understanding on the shape recovery characteristic of SMA under various thermomechanical treatments.

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In one aspect of these treatments concerned, the SMA specimen undergoing repeated thermal cycling under constant stress/strain can lead to the development of stress-assisted two-way memory effect. A spontaneous shape recovery of hot and cold shapes, known as two-way memory effect, is developed upon release of the constrained load. The discovery of these memory effects and the ever-increasing demand for mechatronics miniaturization in aeronautical/electrical/mechanical functions, for instance, has propelled the need for advances in SMA-related metallurgical studies.

In Section 1 of this chapter, some background information on SME is presented, including an outline of solid-to-solid phase transformations between martensite and austenite, martensite twinning and detwinning, and characteristic of stress-strain-temperature relationships.

Section 2 will present some background information on the thermomechanical characteristics of NiTi SMA, in which we restrict our attention on the subject of SATWME and TWME. The chapter will end with detailed description of the research objectives and scope, followed by an overview of thesis organization.

1.1 Shape Memory Alloys

Shape memory alloys (SMAs) are group of metallic materials that possess the ability to memorize a specific shape. This memorization process is captured by the non-diffusive thermoelastic phase transformation between the low temperature phase martensite and high temperature phase austenite. When the material is deformed under fully martensitic state, the deformation proceeds with a detwinning process rather than the conventional dislocation slip mechanism and facilitate complete recovery of strains as high as 8% in NiTi [14, 20]. A given plastic strain starts to

1.1 Shape Memory Alloys

recover as soon as the initial martensite phase enters into an austenite phase by heating and completes the shape recovery when the fully austenitic phase is reached. This example of thermally-induced shape recovery phenomenon is known as the shape memory effect (SME).

Among the various compositions of SMAs, the binary Nickel and Titanium (NiTi) alloy has been of particular interest. It has gained considerable attention from an engineering, medical and scientific community due to its superiority in mechanical and shape recovery characteristics. It is known that the course of shape recovery can be influenced by the thermomechanical treatment applied before, during and after undergoing martensite $\leftrightarrow$ austenite phase transformations. One branch of this treatment in NiTi SMA is called “*training*”. An example of training process involves the shape memory element to experience number of thermal cycles under a constant stress, resulting in the development of stress-assisted two-way memory effect (SATWME). Further, removal of constrained stress and continued with a stress-free thermal cycling results in the two-way memory effect (TWME). Unlike the most one-way SME that exhibits a shape change memorized in the high temperature phase, TWME is capable of exhibiting shape changes in both high and low temperature phases. A trained SMA with TWME is theoretically ideal for many shape memory applications, since it does not require a resetting bias force as it is required for the one-way SME.

It can be pointed out that having good knowledge in the shape recovery characteristic of SATWME is of particular importance, since optimal SATWME leads to an enhanced TWME of both high magnitude and stability [21].

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1.2 Shape Memory Effect

1.2.1 Phase Transformation

An understanding of the microscopic mechanism inherent in shape memory alloys (SMAs) is the essence for understanding the macroscopic shape change and its related phenomena. Broadly speaking, there exists a low temperature phase martensite and high temperature phase austenite in NiTi-based SMAs. Of these alloys concerned, the lattice structure of martensite is viewed as a unique monoclinic B19' formed by the non-basal shear. The austenite lattice, on the other hand, appeared to have an ordered B2 body centered cubic (BCC) structure. Figure 1.1 shows the example of thermally-induced phase transformation occurring between these two main phases, which is demonstrated by the differential scanning calorimetry (DSC) thermogram and the schematics of corresponding lattice structures. In the course of heating process, the

Figure 1.1 A typical DSC thermogram of equiatomic NiTi wire specimen (e.g. specimen weight = 10mg, scanning rate = 5°C/min), accompanied by the schematics of martensite and austenite lattice structure.

1.2 Shape Memory Effect

beginning of martensite: $M \rightarrow$ austenite: A transformation (i.e. reverse transformation) is characterized by the A_s -temperature, while the completion of transformation is characterized by the A_f -temperature. The lattice structure of the shape memory material therefore is said to be fully austenitic above A_f . The intersection of the tangential lines drawn along the DSC curve, which are represented by the dashed lines in the figure, indicates the idealized approximation of A_s and A_f temperatures. Likewise, in the course of cooling process, the beginning of $A \rightarrow M$ transformation (i.e. forward transformation) takes place at M_s -temperature and completes at M_f . On further cooling below M_f the lattice structure remains fully martensitic.

For a conventional NiTi-based alloy, the forward/reverse transformation temperatures are predetermined to be in the following order of increasing temperature: $A_f > A_s > M_s > M_f$.

In addition to the nucleation and growth of martensite, it is possible to have an intermediate phase known as rhombohedral (R)-phase prior to the formation of martensite. The lattice structure of R -phase is somewhat viewed as a distorted cubic shape. Unlike the usual martensitic transformation, R -phase begins and completes its transformation within the very short range of temperature interval and this makes it an ideal candidate for thermal actuator applications. In brief, there are three possible causes for obtaining R -phase: (i) introduction of dislocations; (ii) presence of precipitates; and (iii) addition of third element (e.g. Fe, Al) [22]. The mechanism of R -phase formation and its effect on the shape recovery characteristics of SATWME and TWME will be discussed further in the later chapters.

Figure 1.2 shows a hypothetical sketch of stress-temperature and strain-temperature curves, in which the transformation path illustrates the respective generations of recovery stress and strain during phase transformation. During this

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Figure 1.2 Phase transformations of NiTi illustrated with respect to: (a) stress-temperature curve (generation of recovery stress due to constrained strain cycling); and (b) strain-temperature curve (generation of recovery strain due to stress-free thermal cycling).

transformation, the temperature between heating and cooling process differs typically by 30°C for NiTi (cf. Table 2.1). This temperature difference is commonly termed *hysteresis* and is perceived microscopically as a frictional barrier arising from the interfacial motion during phase transformation. In essence, the degree of hysteresis width [23, 24], as shown in idealized schematics in Figure 1.2, can be defined by a mid-temperature of reverse transformation (from A_s to A_f) minus mid-temperature of forward transformation (from M_s to M_f), i.e. hysteresis width = $(A_s + A_f)/2 - (M_s + M_f)/2$.

It has been described in this section thus far that on one hand the shape recovery due to the SME is realized by thermally-induced phase transformation. The phase transformation, on the other hand, can also be realized by the mere application of external stress under isothermal condition, where operating temperature is held above A_f . Such stress-induced phase transformation is generally termed pseudoelasticity. A transition from the thermally-induced SME to the stress-induced pseudoelasticity, whose shape recovery characteristics are captured in association with stress-strain curve and changes in operating temperature, T , is shown in Figure 1.3. When $T < M_f$,

1.2 Shape Memory Effect

the deformation process via tensile loading is accompanied by a twin movement and reorientation process of martensite variants whose orientation eventually gets aligned into a single preferred variant (Figure 1.3(a)). Similar to the case seen in Figure 1.3(a), loading and unloading at higher temperature but below A_f results in the generation of residual strain (Figures 1.3(b) and (c)). However, this residual strain can be recovered completely (provided that the degree of deformation does not exceed the recovery limit) via heating, as is indicated by the dotted line. Obviously, this recovery phenomena is what we observe as the thermally-induced shape memory effect. When $T > A_f$, a continued deformation via loading causes the initiation of stress-induced

Figure 1.3 Schematics of stress-strain curve for a NiTi alloy, loaded and unloaded under tension at different operating temperature, followed by shape recovery via heating or releasing stress: (a) below M_f (full martensite deformation); (b) between M_f and A_s ; (c) between A_s and A_f ; and (d) above A_f (pseudoelasticity).

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martensite (SIM) transformation and owing much to this remarkable SIM feature, an apparent plastic deformation vanishes and transforms back to its initial autenitic phase via unloading.

Since the objectives of this research focuses primarily on the effects of martensite deformation on the shape recovery characteristic, we shall confine our attention to the case where $T < M_f$. Further description on the martensite deformation mechanism that constitutes a twinning, detwinning and dislocation process will be described in the following sections.

1.2.2 Martensite Twinning and Detwinning

Figure 1.4 shows a typical stress-strain curve of as-annealed NiTi specimen subjected to an isothermal uniaxial tension test at room temperature. At this temperature ($T < M_f$) the specimen is initially in the fully martensitic state having monoclinic lattice (at point *o*). When at this state, the lattice structure contains 100% self-accommodated martensite twins. If an external force is applied in this state, the twin boundaries migrate to reorient themselves with the shearing cooperative movement of atoms [25], resulting in a stack of single rhombus variants. The specimen's shape will change under the influence of external force and by this time the alloy is said to be *detwinned*. The term martensite deformation is recognized as a process of changing martensite variant accommodation structure from self-accommodating martensite to detwinned/reoriented martensite through applied external force [26-28].

As shown in Figure 1.4, the martensite deformation process can be sorted out in the order of four distinctive zones I – IV [29-33]: I) Elastic zone of martensite marked from zero stress to the onset of detwinning (point *o-a*), martensite predominated with self-accommodated martensite twins; II) Partial detwinning zone of martensite

1.2 Shape Memory Effect

Figure 1.4 A typical NiTi martensite deformation process represented in stress-strain curve and its associated microstructural changes.

marked from the onset of detwinning to the sudden increase in stress (point *a-b*); III) Further detwinning zone of martensite marked from the sudden increase in stress to the completion of detwinning process (point *b-c*). The microstructure at this zone contains a fully detwinned martensite and some light dislocations; and IV) Introduction of massive dislocations zone marked from the completion of detwinning process to final fracture (point *c-d*, and beyond point *d* for fracture).

Unloading from point *d* to zero stress level (point *e*) is elastic and leaves behind residual strain of approximately 14% in this example. This implies that the unloading

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process caused an elastic recovery of 4% approximately (i.e. considering that the martensite deformation progressed up to 18% (point *d*) and then unloaded). In this process, the resultant microstructure is an intermixed detwinned martensite and massive dislocations. The generation of dislocations inevitably removes the portion of recoverable strain as in one-way SME. However on the positive side, it creates necessary internal driving force to develop a TWME. By point *f* the alloy has been reloaded to 400MPa stress and constrained at this stress level to undergo thermal cycling, for instance, would guide the growth of martensite variant into preferential orientation to produce higher transformation strains [34]. In view of SATWME and TWME, the key element to this constrained thermal cycling therefore is the magnitude of *constrained stress* applied and the extent to which *martensite deformation* progresses.

It is noteworthy to highlight that the detwinning process observed in zone II progresses with virtually no change in stress values – leading to a generation of *stress-plateau*. The end of stress-plateau does not indicate the end of detwinning process and it requires increased stress to detwin those remaining twinned variants. Hence, based on these unique characteristics the former partial detwinning process is termed *domino detwinning*, whilst the latter further detwinning process is termed *assisted detwinning* [29, 35, 36].

Having unveiled the brief background of martensite deformation process in this section, the detwinning process of martensite is considered one of the most important microscopic deformation mechanisms responsible for the SME. In one respect, the length of the stress-plateau is related to detwinning magnitude and textures in the alloy [36-38]. Previous results [35, 39] suggested that formation of high density of

dislocations due to having insignificant stress-plateau results in a poor one-way and two-way memory effect.

1.2.3 Stress-Strain-Temperature Relationships

As has been discussed in previous sections, the driving force to initiate forward and reverse martensitic transformation can be either thermal or mechanical, or combination of both. In a case of thermally-induced transformation where no external stress is applied, the $M \leftrightarrow A$ transformations can take place solely by heating and cooling. On the contrary, in a case of stress-induced transformation where temperature is held constant above A_f , the sole application of external stress causes the formation of stress-induced martensite from the parent phase (austenite). In this way, for the latter case the driving force for the transformation to initiate/terminate is mechanical as opposed to thermal.

The stress dependence of the main four phase transition temperatures (M_s , M_f , A_s , A_f) is shown in Figure 1.5. Although the stress-temperature relationship is illustrated as strictly linear in the figure, the relationship may well be recorded as nonlinear especially in the lower stress region [40, 41]. Nonetheless, if the specimen's temperature is raised under no load condition, the reverse transformation begins at A_s and completes at A_f . Likewise in this load-free condition, during the subsequent cooling process the forward transformation begins at M_s and completes at M_f . This is the usual phenomena of SME. However, if the specimen is subjected to a constrained stress thermal cycling (i.e. some degree of load (σ_1) is applied at temperature, $T_1 < M_f$, and held constant at this stress level throughout cycling), principally all the four transition temperatures will be increased to M_s' , M_f' , A_s' and A_f' . Contrasted with SME, taking loading path at a temperature, $T_2 > A_f$, produces SIM upon which stress

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Figure 1.5 Stress-temperature phase diagram showing stress dependence on the transformation temperatures.

exceeds beyond critical stress level σ_2 leads to the usual pseudoelastic loop (cf. Figure 1.3(d)).

Considering the above stress-temperature relationships, the stress dependence of the transformation temperatures can be approximated by the Clausius-Clapeyron equation [25, 42]:

$$\frac{d\sigma}{dT} = \frac{\Delta H}{T\epsilon} \quad (1.1)$$

1.2 Shape Memory Effect

where σ is the applied external stress, T is the temperature, H is the transformation enthalpy in per unit volume, and ε is the transformation strain resolved along the direction of the applied stress. In recovery stress experiment (cf. Figure 1.2(a)), the *stress rate*, $d\sigma/dT$, is a very important parameter which determines the functional performance of SMAs under a constraint condition, and is found to increase with increasing magnitude of pre-strain, ε [43].

In addition to Clausius-Clapeyron equation, the stress-strain-temperature relationships of SMA and its associated kinetics of forward/reverse transformations can alternatively be expressed by the phenomenological constitutive equation [44]:

$$\dot{\sigma} = D\dot{\varepsilon} + \Theta\dot{T} + \Omega\dot{\xi} \quad (1.2)$$

where stress, strain and temperature (σ , ε and T) are represented in the rate form indicating the time derivative, D , Θ and Ω are the material constants obtained by experiment, and ξ is the martensite ratio, which is also represented in the rate form. In general, Tanaka's model represented in equation (1.2) is a useful model to replicate the one-dimensional thermomechanical behavior of SMA.

1.3 Thermomechanical Behavior of NiTi SMA

1.3.1 Training Procedure

The shape remembered by thermomechanical training process is that of both martensite and austenite phase, and in this sense its consequential shape recovery phenomena are often called two-way memory effect (TWME). Although various training procedures causing TWME have been proposed and investigated (cf. Table 2.3), it is our primary interest to pay particular attention to the training procedure

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Figure 1.6 Schematic illustration of training procedure that leads to the development of SATWME and TWME.

involving constrained stress thermal cycling and free recovery. Such training procedure is presented schematically in Figure 1.6. The ability of specimen to demonstrate two-way shape recovery under stressed cycle (i.e. corresponds to a cooling-heating path drawn in the strain-temperature plane, highlighted in light grey color) is known as stress-assisted two-way memory effect (SATWME).

1.3.2 Stress-Assisted Two-Way Memory Effect (SATWME)

In a constrained stress thermal cycling, a formation of martensite variants upon cooling (i.e. represented by the bold blue dashed line in the stressed plane, as shown in Figure 1.6) is supported by the external stress, resulting in the generation of relatively large transformation strain. Following the cooling process, a reversible shape recovery takes place by means of heating to above A_f . This leads to the completion of 1st training cycle where development of SATWME yields. Figure 1.7(a) illustrates the evolution of SATWME, which is captured from the strain-temperature

1.3 Thermomechanical Behavior of NiTi SMA

Y-Z axis of Figure 1.6. The functional performance of SATWME can be evaluated in terms of strain value, ε_{SATW} , which is in the order of about 5 to 8% for Ni-Ti [21, 24, 41, 45-52] and Ni-Ti-Cu alloys [51-55]. The value of ε_{SATW} is, by and large, influenced by the thermomechanical treatments: magnitude of martensite pre-deformation and constrained stress, combinations of annealing, ageing and cold-work applied prior to thermal cycling, and so on. Other influencing factor also includes the number of thermal cycling repeated before unloading to zero stress level. With increasing number of cycles, the values of ε_{MA} and ε_{IR} changes in conjunction with the upwardly shift of strain-temperature curve [47, 49, 51, 53, 56]. Furthermore, recent experimental investigation [57] revealed that the value of ε_{MA} is strongly connected to the propagation of martensite deformation, making it an important parameter capable of predicting the magnitude of SATWME. The value of ε_{IR} , on the other hand, is suggested to be connected to the amount of dislocations introduced during training and is partially responsible for the development of TWME [21].

1.3.3 Two-Way Memory Effect (TWME)

The current understanding of the development mechanism of TWME is twofold: in one aspect, the memory effect is related to the preferred orientation of the growing martensite plates that are guided by the internal stress fields introduced by plastic deformation of martensite and/or of austenite matrix during training. For the other aspect, the presence of locally stabilized martensite plates retained above A_f is considered responsible for TWME [58, 59]. The stabilized martensite is believed to suppress the self-accommodating nature of martensite plates, whereby providing an internal stress field for the nucleation and growth of the selected variants on cooling.

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Figure 1.7 Schematic illustration of strain-temperature curves extrapolated from the stress-strain-temperature diagram of Figure 1.6: (a) the development of SATWME and labeling of various strains: $SATW$, stress-assisted two-way memory strain; IR , irrecoverable strain; MA , martensitic strain; and (b) the development of TWME via unloading (elastic recovery) and stress-free cycle: TW , two-way memory strain.

Irrespective of the two aspects mentioned, the preferential formation of specific martensite variants induces a reversible macroscopic shape change of the alloy (Figure 1.7(b)). Hence, TWME appears repeatedly in multiple thermally-induced phase transformations provided that the microstructural configurations remain unaffected.

1.3.4 Correlation between SATWME and TWME

It has been discovered that the SATWME and TWME are prone to show macroscopic correlation in their recovery strain magnitudes [60, 61]. The magnitude of stress-assisted two-way memory strain, ε_{SATW} , increases to its maximum value with increasing martensite deformation and declines after further increase in deformation. This trend is directly reflected in the magnitude of two-way memory strain, ε_{TW} . Recent results [62] also confirmed the direct correlation of these memory strains, though it was found that the correlation would become no longer valid if certain

1.3 Thermomechanical Behavior of NiTi SMA

conditions of partial transformation are imposed during training. That is, when the specimen is subjected to optimum magnitudes of martensite pre-deformation and constrained stress, undergoing partial reverse transformation under constraint causes significant decrease in ε_{SATW} , but causes almost no change in ε_{TW} . In effect, some fractions of martensite variants are retained due to partial reverse transformation. The influence of retained martensite on the recovery strain on one hand has been claimed to assist the TWME [58]. On the other, the retention of martensite caused by the locking mechanism of dislocations has been claimed to decrease the amount of recoverable strain in constrained thermal cycling [51] and pseudoelastic cycling [63]. The issues concerning retention of martensite will be further addressed in Chapters 5 and 7.

1.3.5 Partial Transformation

Previous shape recovery results [64, 65] demonstrated that the effect of partial transformation on the transformation temperatures is prominent on the start of transformation (i.e. M_s , A_s temperature) than the completion of transformation. That is, the trace of the forward/reverse transformations after partial transformation ends precisely on the main fully transformed loop. Another feature noteworthy of partial transformation is that of multiple-step transformation (MST). In a calorimetric measurement, MST appears in the fully transformed calorimetric heating path following a partial reverse transformation imposed between A_s and A_f temperatures [66-75]. What is more out of the ordinary is that the NiTi alloy seems to have the ability to memorize its so-called arrested temperature imposed between A_s and A_f , i.e. a kinetic stop temperature that separates the MST is closely related to the previous arrest temperature [67, 68, 71]. The MST is observed to be a one-time only event that

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the endothermic multiple-peaks induced by the partial transformation will be erased during the next heating cycle, reverting back to its original single peak.

The partial reverse transformation initiated under constrained [76] and unconstrained condition [77] also resulted in the generation of MST, in which the transformation occurring at higher temperature was attributed to the postponed memory effect of retained martensite. Other partial transformation process under constrained condition may include partial forward transformation [78]. However, considering the fact that TWME is dependent on the preferential orientation of martensite variants [2, 13, 79-81] that are essentially guided by the internal stress fields [82-87], focus is given on the partial reverse transformation in this research for two reasons: i) to investigate the effects of introducing two distinctively oriented martensite variants (i.e. stress-assisted and retained detwinned/reoriented variants) on SATWME and TWME; and ii) to investigate the effects of internal stress formed by the accommodation process of stress-assisted and retained variants on SATWME and TWME.

As will be shown later in Chapter 7, the martensite variant configurations established by full/partial transformation form the basis of the underlying microstructural mechanisms responsible for SATWME and TWME.

1.4 Research Objectives

A spontaneous shape change of TWME is truly fascinating due to its extraordinary ability to remember both high and low temperature shapes without the need of resetting bias forces. Inspired by the works of Stalmans et al. [60, 61] in which they demonstrated a recovery strain correlation between SATWME and TWME to the number of training cycles, the present research was conducted under both full and

1.4 Research Objectives

partial transformation conditions to further discuss the underlying micro- and macroscopic mechanisms responsible for these memory effects.

The primary goals of this work are twofold: *the first is to identify the predominant factors influencing on the shape recovery characteristics of SATWME and TWME; and the second is to further clarify on the thermomechanical correlation between these memory effects to martensite deformation via experimental and macromechanical approaches.*

The motivation for carrying out further investigation on the SATWME, firstly is to establish conditions for achieving maximum recovery strain as a function of: i) martensite deformation (i.e. taking into account the degree of deformation applied prior to thermal cycling and its propagation due to cycling); ii) constrained external stress; and iii) developed internal stress. In general, thermomechanical training process creates an internal stress field, which is manifested by the progressive shift of M_s -temperature. The magnitude of internal stress can be estimated by the Clausius-Clapeyron-like macromechanical model [53]. Secondly, anisotropy of internal stress is often emphasized in the TWME, but to the present author's knowledge to date, there has been no decisive experimental/macromechanical evidence reported in the academic literature.

In addition to unfolding the critical role of internal stress in causing the SATWME and TWME, another mechanism responsible for TWME, namely the role of a local stabilization of martensite (retained above austenite finish temperature) needs to be clarified. It has been suggested that on one hand the amount of retained martensite increases as the number of training cycle increases [58]. These retained martensites are claimed to favor in the development of TWME. On the other, Stalmans et al. pointed out that those martensite remnants could be erased once

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overheated above A_f -temperature and show only a minor effect on the TWME [61]. More recent work by Miller and Lagoudas [51] has demonstrated that increasing fraction of retained martensite results in higher plastic strains with lower TWME.

Research is still ongoing to clarify the debatable views on the influence of retained martensite on the development of TWME. Hence, one's exploration begins.

1.5 Scope of Work

The shape recovery characteristics of NiTi alloy are greatly influenced by the composition, the thermomechanical treatment such as cold-work, annealing and ageing, together with the large number of stress-strain-temperature parameters. The texture and orientation dependence of recoverable strain also exists. Indeed, this makes a characterization of NiTi alloy extremely challenging and time consuming for generating experimental data.

Given these facts and the research objectives put forward, we have centralized our attention on the particular thermomechanical training procedure, as shown in Figure 1.8. Each of the procedure flows through from left to right until the development of TWME. To begin with, pre-thermomechanical treatments such as composition (at. %), cold-work (reduction %), and annealing (temperature, duration) are all fixed. Following the preparatory stage, the martensite deformation proceeds with respective magnitudes of pre-strain and constrained stress that are defined as variable. Another variable considered in the course of thermal cycling process is the full/partial cycle and the number of repeated cycles. With the thermomechanical features displayed in SATWME, the shape recovery characteristics of TWME will be examined and further cross-examined by thermodynamic analysis. Details on the

1.5 Scope of Work

Figure 1.8 Scope of Experimental Work.

experimental work, along with the analytical work and modeling are described as follows.

1.5.1 Experimental Work

The compositions of NiTi SMA can vary approximately between 49 and 51 at% Ni [14] or 48 and 52 at% Ni [20]. With this variation in composition not only modifies the mechanical properties but also the transformation properties of the alloy, including transformation temperatures (M_s , M_f , A_s , A_f) and hysteresis [88]. However, by taking into account the operational temperature range of the experimental apparatus (-70 ~ 250°C) [89] and ease of availability in the ready-made wire form, a near equiatomic NiTi alloy was chosen for this experimental work.

There are many well-documented articles that deal with the effect of cold-work and annealing on the various aspects of shape recovery characteristics pertaining to one-way SME, TWME or SATWME [45, 90-94]. Nevertheless, little has been explored for the combined effects of martensite pre-deformation and constrained stress as well as the nature of thermal cycling on the SATWME and TWME. For this

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reason, it is targeted to design a systematic testing program that incorporates those aforementioned mechanical conditions (i.e. pre-deformation, constrained stress) and thermal conditions (i.e. full/partial transformation, number of repetitive cycles).

The obtained quantitative data will allow us to determine the predominant factors responsible for the maximum development of SATWME and TWME. In particular, we will pay close attention to the changes in martensitic strain (i.e. total strain deformation) achieved during constrained cooling and, M_s as a function of constrained stress and number of training cycles. The relation of M_s versus external stress constructed for each training cycle can lead us to the estimation of internal stress. The nature of thermal cycling includes the various degrees of partial reverse transformation imposed between A_s and A_f temperatures under constraint. This amounts to quantifying the effect of retained martensite on the SATWME and the subsequent development of TWME. In view of training cycle, our testing program precludes the SIM cycling since our interest for the most part lies in evaluating the correlation of SATWME and TWME. Hence, the possibility of including constant strain cycling is dismissed in this work.

With the collection of experimental data and having interpreted them with the help of previously reported literatures (especially in the area of microstructural observations) would yield invaluable new knowledge that shine a light on the mystery of TWME.

1.5.2 Analytical Work and Modeling

A thermodynamic analysis, by means of differential scanning calorimetry technique is then applied to the post-trained specimens. This technique provides us with the thermodynamic properties including transformation temperatures, interval and

1.5 Scope of Work

enthalpy, and temperature hysteresis. In essence, these properties are the definitive experimental parameters capable of outlining the thermoelastic characteristics of NiTi alloy.

In this work, we will employ some of the thermodynamic analysis carried out by Ortin and Planes [95, 96], and of which analyzed further by Mari and Dunand [97] to decompose the calorimetrically measured transformation enthalpy into the chemical and non-chemical components. This non-chemical component constitutes the elastic, frictional and defect energies. The storage and release of elastic strain energy generated by the transforming material is of particular importance, since it is closely related to the generation of internal stress. Berveiller et al. [98] defined a relationship between internal stress and stored energy associated with martensitic transformation. Meanwhile, Patoor et al. [99] set forth a micromechanical interpretation of internal stress effect. We will base our internal stress analysis on these models to provide concrete explanation on the thermomechanical correlation of SATWME and TWME.

In the aspect of modeling, the dislocations model of Mitchell [100] and the dislocation pile-up theory reviewed in [101, 102] will be combined to account for the degradation in SATWME due to partial reverse transformation. A schematic model will be proposed in the meantime to illustrate the development of internal forward and back stress. It will be shown that the nucleation and growth of stress-assisted martensite in the presence of retained martensite under constrained cooling causes anisotropy in the internal stress formations. The back stress formation will be based on the works of Mori and Tanaka [103], Mura [104], and Sun and Hwang [105, 106]. In effect, clear understanding on the internal forward and back stress formations will shed a light on the microstructural mechanisms operating behind the TWME.

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1.6 Thesis Organization

The structure of this thesis is organized into eight chapters.

The thesis has begun in writing from introductory section in Chapter 1. The text proceeded from the description of shape memory alloy and its related shape memory phenomena to the mechanism of shape memory effect and thermomechanical characteristics of NiTi shape memory alloy. The objectives and scope of this research were highlighted towards the end.

In the review section of Chapter 2, it is attempted to give comprehensive overview on the progressive research and development of shape memory alloys, shape recovery characteristics, thermomechanical training, and thermodynamic and macromechanical analysis.

Chapter 3 describes the experimental setup and procedure in detail. This includes the setup of Instron-type Microforce Testing System and the differential scanning calorimetry machine used to obtain results during training and after training, respectively.

Chapter 4 includes the evaluation on the shape recovery characteristics of SATWME under fully transformed condition. The experimental results were, by and large, evaluated in terms of stress-strain, stress-temperature and strain-temperature relationships with respect to three different test conditions applied. Other evaluation also includes the development of internal stress. The shape recovery correlation between SATWME and TWME will be outlined in terms of martensite deformation progressed and internal stress developed during training. Meanwhile, the experimental findings will be discussed by relating them to the previous studies and analysis.

Chapter 5 mainly includes the strain-temperature evaluation on the shape recovery characteristics of SATWME and TWME under partially transformed

1.6 Thesis Organization

condition. Similar to the case of full transformation, the results concerning the three different thermomechanical conditions of fixed pre-strain and constrained stress, and continued number of training cycles will be presented. Based on the summarized results of M_s -temperature versus retained martensite, we will make an attempt to explain the effects of internal forward and back stress formations on the SATWME and TWME.

Chapter 6 presents the thermodynamic analysis carried out on the post-trained specimens. We make use of thermodynamic balance equations to interpret the changes in transformation temperatures and enthalpies, and temperature hysteresis generated upon experiencing different fully transformed training conditions. The effective decrease of transformation enthalpies will be further analyzed via transformation enthalpy formulations.

In Chapter 7, the mechanism of two-step transformation will be examined by adopting macromechanical and thermodynamical approaches: i) strain comparison; and ii) DSC analysis on incomplete reverse transformation. The analysis on pre-positioning and overheating phenomena of two-step reverse transformation will be made in light of elastic strain energy mechanism and transformation temperature interval. The strain-temperature results will then be compared with the calorimetric measurements to provide further insight into the mechanism of two-step reverse transformation. The highlight of Chapter 7 will be the two-step transformation model. It presents the current understanding of the theoretical illustration of dislocation pile-up, internal stress formations and cross-slip mechanism (relaxation of plastic deformation).

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Finally in Chapter 8, an overall summary of the thesis and conclusive remark drawn from the present experimental and macromechanical works will be presented, followed by a description of future research work issues.

CHAPTER 2

Literature Review

In a few decades, the shape memory effect and associated phenomena such as pseudoelasticity, all round shape memory effect and two-way memory effect have attracted enormous interest amongst researchers. In this chapter of the thesis, firstly, historical issues of SMA will be presented, followed by a brief presentation of the previous work related to shape recovery characteristics. The literatures pertaining to the present research – thermomechanical training and its resultant memory effect, discussion on the thermodynamic and macromechanical analysis – will be presented in the meantime.

More detailed presentation of the most relevant literatures to this research will be sought throughout the thesis.

2.1 Discovery of Shape Memory Alloys

SMA history goes back to early 1930s when Swedish physicist Arne Olander first discovered the shape memory effect (SME) using a binary alloy of Gold-Cadmium [107]. In 1954 Basinski and Christian observed rubber-like elasticity in the Indium-Thallium alloys [108]. Wilson, in 1939, observed the order-disorder transformation behavior under hydrostatic pressure in a Cu-based alloy Cu-Zn [109]. He also

CHAPTER 2. Literature Review

investigated the pressure-temperature relationships of Cu-Au alloy. The recognition of SMA rapidly boosted after when in 1962, William J. Buehler from U.S. Naval Ordinance Laboratory discovered the SME in a binary alloy of NiTi [110]. Henceforth, research into the metallurgy and potential applications of SMA commenced in earnest.

This newly discovered alloy, NiTi (Nitinol), was found to be highly bio-compatible, non-toxic, and can be manufactured at lower cost than the previously discovered SMAs (e.g. AuCd). Much dedicated study of Nitinol's crystal structures and material properties has resulted in the emergence of SMA engineered products: SMA shrink-to-fit hydraulic pipe couplings [111], thermal mixing valve control unit [112], air flow control for an air conditioner [40, 112], eye glass frames [113], medical and dental implants to list a few [114]. A comprehensive overview of non-medical and medical SMA applications is well documented in the following literatures [17, 18, 115-117].

With the increased dedication to a fundamental research of SME, a number of other metallic alloy systems that exhibited shape memory phenomena were investigated. Table 2.1 lists the example of these systems with some details of their microstructural and transformation characteristics. Of these alloy systems listed, however, the Nitinol and a few of other Cu-based alloys (e.g. Cu-Zn-Al and Cu-Al-Ni) have received the most development effort and commercialization exercise. Their general properties listed in [14] are summarized in Table 2.2.

The customary compositions of Nitinol is equiatomic (i.e. 50 atomic-% Ni / 50 atomic-% Ti) but a small atomic-% of copper, iron, cobalt, or chromium can be substituted for Ni or Ti to produce a ternary alloy.

2.1 Discovery of Shape Memory Alloys

Alloy	Composition (atomic – %)	*Structural change	Temperature hysteresis (K)	Ordering
Ag-Cd	44-49 Cd	B2 → 2H	~ 15	Ordered
Au-Cd	46.5-48.0 Cd	B2 → 2H	~ 15	Ordered
Cu-Zn	49-50 Cd	B2 → trigonal	~ 2	Ordered
	38.5-41.5 Zn	B2 → M(modified) 9R	~ 10	Ordered
Cu-Zn-X (X = Si, Sn, Al, Ga)	A few at. %	B2 → M9R	~ 10	Ordered
Cu-Al-Ni	28-29 Al, 3.0- 4.5 Ni	DO ₃ → 2H	~ 35	Ordered
Cu-Sn	~ 15 Sn	DO ₃ → 2H, 18R	-	Ordered
Cu-Au-Zn	23-28 Au 45-47 Zn	L2 ₁ → M18R	~ 6	Ordered
Ni-Al	36-38 Al	B2 → 3R, 7R	~ 10	Ordered
Ti-Ni (Nitinol)	49-51 Ni	B2 → monoclinic	~ 30	Ordered
		B2 → R-phase → (monoclinic)	~ 2	Ordered
Ti-Ni-Cu	8-20 Cu	B2 → orthorhombic → (monoclinic)	4 ~ 12	Ordered
Ti-Pd-Ni	0-40 Ni	B2 → orthorhombic	30 ~ 50	Ordered
Fe-Pt	~ 25 Pt	L12 → ordered BCT	~ 4	Ordered
In-Tl	18-23 Tl	FCC → FCT	~ 4	Disordered
In-Cd	4-5 Cd	FCC → FCT	~ 3	Disordered
Mn-Cu	5-35 Cu	FCC → FCT	-	Disordered
Fe-Pd	~ 30 Pd	FCC → FCT	-	Disordered

*Structural change observed upon martensitic transformation (i.e. cooling).

Table 2.1 List of SMAs exhibiting shape memory effect and pseudoelasticity [13, 118].

Although Nitinol is about four times the cost of Cu-Zn-Al alloys, it possesses several advantages over Cu-Zn-Al and Cu-Al-Ni: greater flexibility, excellent corrosion resistance and biocompatibility, and produces larger recoverable strain. Nitinol is also known to exhibit excellent mechanical damping capacity, offering better opportunities in the damping applications compared with Cu-Zn-Al [17]. As a consequence, the present research will concentrate on the further understanding of

CHAPTER 2. Literature Review

Properties	NiTi	Cu-Zn-Al	Cu-Al-Ni
• Melting Temperature (°C)	1240-1310	950-1020	1000-1050
• Density (g/cm ³)	6.40-6.52	7.64-8.0	7.1-7.2
• Thermal conductivity 20°C (W/mK)	10-18	120	75
• Coefficient of thermal expansion (10 ⁻⁶ /K)	6.6-10	17	17
• Corrosion resistance	similar to 300 series stainless steel or Ti	similar to aluminum bronzes	similar to aluminum bronzes
• Biological compatibility	excellent	bad	bad
• Young's modulus (GPa)			
i) Austenite	70-98	70-100	80-100
ii) Martensite	27		
• *Shape recovery properties:			
i) One-way SME (%)			
$N < 10^2$	6-8	4	4
$N < 10^5$	2		
$N < 10^7$	0.5		
ii) Two-way SME (%)			
$N < 10^2$	6	1	1.2
$N < 10^5$	2	0.8	0.8
$N < 10^7$	0.5	0.5	0.5
iii) Max. recovery stress (MPa)	600-800	500-700	600

* The symbol N represents the number of cycles undergone.

Table 2.2 Summary of property values for NiTi, Cu-Zn-Al and Cu-Al-Ni [14].

two-way shape recovery characteristics of near equiatomic NiTi alloy.

2.2 Shape Recovery Characteristics

The basis of the shape recovery characteristics manifested in SMAs is the martensitic phase transformation. In metallurgical study [119, 120], it is generally perceived as a first order, diffusionless and thermoelastic transformation where atomic movements during the phase change are insignificant. Further, the martensitic transformation on cooling progresses with the continuous nucleation and growth of martensite plates. On heating, the shrinkage and disappearance of martensite plates occur under a balance

2.2 Shape Recovery Characteristics

between thermal and elastic effects. As a result, the transformation is observed to be reversible and thermoelastic.

The most widely recognized shape recovery characteristics of SMAs include, SME and pseudoelasticity. The former characteristic is associated with the thermally-induced reversible phase change between martensite (a lower symmetric structure) and austenite (an ordered cubic structure), whereas the latter characteristic is associated with the formation of reversible stress-induced martensite at high temperature.

2.2.1 Shape Memory Effect (SME)

This thermomechanical behavior requires a specimen to be deformed in the martensite condition, i.e. the operating temperature is set below martensite finish temperature, M_f . Below M_f , the specimen's microstructure consists of martensite variants (self-accommodated twins) and the physical properties change upon starting or finishing martensitic phase transformation. Figure 2.1(a) illustrates a typical stress-strain curve of SMA under tensile deformation of such condition. A schematic example of SME that corresponds with loading, unloading and shape recovery demonstrated in the stress-strain curve is represented in a coiled spring, as shown in Figure 2.1(b). For a NiTi, the residual strain on the order of 6 to 8% generated after unloading to zero stress level can be recovered completely upon heating. The recovery process of the specimen reverting back to its original shape stems from the reverse transformation in the material [121].

Wayman and Duerig [42] illustrated the geometrical concept of microstructural changes between martensite and austenite. The structural changes were typically characterized by the four main transition temperatures: A_s , A_f , and M_s , M_f , defined as

CHAPTER 2. Literature Review

Figure 2.1 A typical SMA mechanical behavior in tension and its associated SME: (a) stress-strain curve of a shape memory specimen in fully martensitic state; and (b) schematic of a coiled spring exhibiting SME.

austenite and martensite start, finish temperatures arranged in the order of heating and cooling process, respectively [25, 42]. When lattice structure is found to be 100% martensite, each variants of martensite¹ are self-accommodated and their orientations are twinned and symmetric about twin boundaries², as illustrated in Figure 2.2. Upon deformation via external force, the twin boundaries migrate to reorient themselves without changing lattice symmetry – by this time the alloy is said to be ‘*detwinned*’. Detwinned martensite lattice structure remains unchanged until heated to A_s , where deformed shape start to go back to its original shape through a reverse transformation. The formation of austenite is completed when A_f is reached and without undergoing any shape change, the lattice structure transforms back to 100% twinned martensite when cooled to below M_f through a forward transformation.

For the past four decades, there has been considerable progress in understanding the origin and the transformation mechanism of SME. A pioneering work goes back to 1965 when Wang et al. [122] conducted the X-ray diffraction study of NiTi single

¹ Lattices having energetically equivalent configurations are called variants. In general, there are up to 24 types of martensite variants exist in SMAs [2, 121].

² It is a mirror plane of arranged atoms: an atom located on the twin boundary shows reflected mirror images left and right of the boundary [42].

2.2 Shape Recovery Characteristics

Figure 2.2 Illustration of a shape memory process in microscopic-level.

crystals. In their work, it was observed that the crystal structure is not a simple CsCl-type and is distinct from other SMAs such as In-Tl, Cu-Al, and Au-Cd. They also outlined in their later study [123] the crystal structure of higher temperature phase (austenite) and that of lower temperature phase (martensite) to be identified as cubic B2-type and triclinic (P1) hexagonal (P6/m)-type, respectively. Explanation on the nature of SME was addressed by de Lange and Zijderveld [124]. They suggested that the martensitic transformation occurs due to deformed martensites which are preferentially oriented with respect to the direction and the sign of mechanical stress. With their hypothetical schematics, they also postulated that a different texture of martensite would be formed under tensile and compressive loadings.

Along with the studies of NiTi based alloys, pioneering study on the crystallography and the nature of martensitic transformation in a Cu-based alloy

CHAPTER 2. Literature Review

includes the works of Massalski and King [125], Nishiyama and Kajiwarra [126, 127], Swann and Warlimont [128], Duggin and Rachinger [129], and Otsuka and Shimizu [130, 131]. Otsuka further attempted to firmly explain the origin of memory effect based on the electron and optical microscopic observations [5]. He proposed two basic requirements for the memory effect: i) the martensitic transformation is thermoelastic; and ii) the shear mechanism (observed as a lattice invariant strain) in martensite phase is not dislocations but twins.

In 1975 Wayman attempted to put together a better understanding of martensite deformation (analysis on stress-strain curve, samples deformed in tension below M_f), shape memory and related mechanisms [132]. He emphasized that, for a polycrystalline material, the randomly oriented variants reorient themselves into single preferred variant via deformation is a necessary process for SME. When dealing with thermomechanical nature of SMA, although there remains much controversial argument for estimating the equilibrium temperature, T_0 , where the amount of chemical free energy is balanced by the counterpart [133, 134], Tong and Wayman concluded that the value of T_0 can be formulated by the following relation:

$$T_0 = \frac{1}{2}(M_s + A_f). \quad (2.1)$$

This equilibrium temperature is affected by the applied and developed stresses during a martensitic transformation. The Clausius-Clapeyron like relation [135] clearly represents the effect of stress, σ , on the equilibrium temperature, T_0 , between austenite A and martensite M :

2.2 Shape Recovery Characteristics

$$\frac{dT_0^\sigma}{d\sigma} = \frac{\varepsilon^{A-M} T_0}{\rho \Delta H^{A-M}} = \frac{\varepsilon^{A-M}}{\rho \Delta S^{A-M}} \quad (2.2)$$

where ε^{A-M} is the transformation strain, ρ is the density of the material, and the thermodynamic properties ΔH^{A-M} and ΔS^{A-M} are the transformation enthalpy and entropy, respectively, detected at T_0 . In 1976 Warlimont provided a brief overview on SME, covering some of the important shape memory aspects pertaining to nucleation and growth of martensite plates, twinning and reorientation mechanism of martensite [136]. A comprehensive overview on the SME behaviors is also found in a number of literatures published [2, 13, 14, 25, 118, 137-139].

2.2.2 Pseudoelasticity (PE)

When the thermoelastic martensite transformation is coupled with an external stress, other unique shape recovery phenomenon known as pseudoelasticity (or superelasticity) is observed. To date, there are number of shape memory materials capable of exhibiting this unique phenomenon, e.g. In-Tl, Au- and Ag-based alloys, a number of Cu-based alloys, and NiTi-based [140]. As illustrated in Figure 2.3, a shape memory specimen deformed beyond its apparent yield point fully recovers its original shape upon unloading due to the reversible nature of the transformation. This reversible nature arises from the formation of stress-induced martensite (SIM) during loading and the reversion to initial austenitic structure via unloading. The temperature range within which the PE can be manifested is $A_f < T < M_d$ (i.e., at above M_d , no stress-induced martensite is formed) [141]. The enclosed area of pseudoelastic loading-unloading hysteresis loop (E_D) represents the amount of dissipated strain energy, while the area under the unloading curve represents the amount of recoverable

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Figure 2.3 A typical superelastic response under tension and its associated shape change: (a) stress-strain curve of a shape memory specimen in fully austenitic state; and (b) schematic of a coiled spring exhibiting superelasticity.

strain energy (E_R) [142]. The values of these strain energies generated in SMAs are exceptionally large compared with those of conventional metals in the region of recoverable deformation. It is precisely because of this remarkable efficiency for energy storage (defined as $E_R/(E_D + E_R)$) [143] could make SMA a suitable candidate for the damping and seismic applications, as well as vibration control in other applications.

2.2.3 Thermomechanical Response of SMA

The magnitude of recoverable strain manifested in SME and PE is found to be heavily dependent on the composition [88, 144-146], thermomechanical treatment such as cold-work, annealing and ageing applied before, during or after phase transformations [45, 90-92, 144, 147-149] as well as the magnitude and constraint of externally applied stress-strain-temperature combinations [44, 150-153]. Meanwhile, it has been found that the response is strongly dependent on texture [37, 38, 154-157] and crystal orientations [25, 158-161].

2.2 Shape Recovery Characteristics

Much of the experimental works thus far have been dedicated to understand the intricate shape recovery mechanism of thermally-induced SME and stress-induced PE. A comprehensive investigation of SME and SIM cycling, and its resultant two-way shape recovery characteristics are given in the works of Wayman [121, 132, 162], Perkins [163, 164], Perkins and Sponholz [58], Adachi and Perkins [165], Perkins et al. [166] and Stalmans et al. [60, 61] to name a few. They investigated the shape recovery dependence on the characteristic of martensite deformation, which is essentially connected to an evolving microstructural configuration and reconfiguration.

2.3 Thermomechanical Training

The spontaneous shape recovery of two-way memory effect (TWME) is not an inherent property of SMAs and requires thermomechanical training. In early 1970s saw the first of its kind discovery of TWME in the severely deformed SMAs such as NiTi [167], Ni-Al [168], Cu-Zn [168, 169], Cu-Zn-Ga [79], and Cu-Zn-Al-Ni [82]. In 1974, based on the observations of mechanical behavior, Perkins attributed TWME to the development of residual stresses that are imparted by the martensite deformation and incomplete one-way SME [170].

Following these pioneering works, in recent years there has been a discovery and investigation of various training procedures, in effort to develop a TWME of both high magnitude and stability. These procedures include but not limited to: i) performing a severe plastic deformation of heat-treated shape memory specimen in the martensitic state followed by free thermal recovery; ii) thermal cycling under constant stress; iii) stress-induced martensite (SIM) transformation under constant temperature; iv) constrained ageing; and v) combination of SIM and SME cycling. Table 2.3 summarizes these training procedures in the aforementioned order i) – v)

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with schematics of relevant stress-strain and strain-temperature curve, along with the corresponding references. It can be seen that the training procedure involves the formation of SIM or reoriented martensite variants via respective pseudoelastic or martensite deformation. In addition, other than forming particular martensite variants, the formation of oriented precipitates via constrained ageing training method (also known as stabilized SIM training method [84, 171-177]) has been found effective to obtain TWME, especially for Cu-based alloys.

Training procedure	1) Stress-strain curve	2) Strain-temperature curve	Reference
i) Martensite deformation + free recovery			[79, 80, 82, 169, 170, 179, 180, 182-185]
ii) Constrained stress thermal cycling + free recovery			[21, 46, 47, 56, 60, 186-191]
iii) SIM cycling + free recovery			[180-182, 186, 192]

Table 2.3 Example of various training procedures for developing a TWME; solid/dashed black line represents mechanical loading, unloading or reloading processes, solid/dashed red and blue lines represent heating and cooling process, respectively.

2.3 Thermomechanical Training

iv) Constrained ageing + free recovery			[83, 84, 171-177, 193-196]
v) Combination of SIM and SME cycling + free recovery	<p>(*Cooling down to below M_f while holding the stress constant, after which unload to zero stress.)</p> <p>or</p> <p>1) Heating ($T > A_f$) 2) Cooling ($T < M_f$) 3) Cooling ($T < M_f$) 4) Heating ($T > A_f$) 5) Cooling ($T < M_f$) 6) Heating ($T > A_f$)</p>		[48, 58, 197]

Table 2.3 Example of various training procedures for developing a TWME (continued).

Research into the mechanism of TWME has shown that plastic deformation of martensite is a necessary prerequisite condition for developing a TWME [166, 168, 169, 178]. Furthermore, some of the earlier research has yielded the common understanding that in microscopic-scale, the TWME originates from specific form of

CHAPTER 2. Literature Review

internal stresses and dislocation structures that were generated by the training process [58, 83-85, 178-181].

In a certain training process, the magnitude of shape recovery is observed to be dependent on the magnitude of one-way memory strain [21, 49, 60, 191]. The macroscopic observations [60, 61] also indicated that there seems to be an intrinsic correlation between SATWME and the subsequent development of TWME.

2.4 Thermodynamic and Macromechanical Analysis

In the first-half of 1970s, a general thermodynamic framework that deals with the thermoelastic martensitic transformations was proposed by Tong and Wayman [133, 198], and Olson and Cohen [199]. Their formulations were mainly based on a concept of local energy balance between chemical and non-chemical contributions. A chemical energy contribution stems from the difference in Gibbs free energy between austenite and martensite phase, which act as a driving force to promote whichever phase with lower energy at each high/low temperature. In 1979, Salzbrenner and Cohen attempted to describe the non-chemical contribution by considering the stored elastic strain energy (elastic accommodation of transformational shape and volume changes) and frictional work (production of internal interfaces motion) [134]. They discussed on the basis of fundamental thermodynamic principles. That is, the measured latent heat accompanying a thermoelastic transformation can be governed by the additive form of chemical and non-chemical components:

$$\Delta H_{net} = \Delta H_{ch} + \Delta H_{el} + \Delta H_I \quad (2.3)$$

where ΔH_{net} is the total transformation enthalpy measured by calorimetry

2.4 Thermodynamic and Macromechanical Analysis

method, ΔH_{ch} is the chemical transformation enthalpy, ΔH_{el} and ΔH_f are the transformation enthalpies arising from the stored elastic energy and the internal frictional work, respectively. Ortin and Planes later extended their work in estimating the elastic energy and frictional work; the estimations were graphically represented by the area of the hysteresis cycle, plotted with entropy change of the specimen as a function of temperature [95]. In the meantime, they conducted thermodynamic analysis taking into account the realistic experimental situations such as thermally-induced transformation under constant stress or strain, and stress- or strain-induced transformation under constant temperature [96].

With reference to the thermodynamic analysis formulated by Ortin and Planes, a number of calorimetric investigations have been conducted [97, 200-206]. While the elastic and frictional energies were both found to increase with the repeated number of martensite: $M \leftrightarrow$ austenite: A cycles [201], the elastic energy was found to decrease with samples with larger grain size [203] and with higher Cu content in TiNi-based ternary alloy [206]. Increased cold-work, on the other hand, accumulates the elastic energies that are stored in the accommodated martensite variants and this stored energy reduces the measured net transformation enthalpy during the reverse $M \rightarrow A$ transformation [202]. In effect, thermodynamic analysis is a useful guide to better one's understanding on the subject of shape recovery phenomena that are essentially connected to a production of reversible effect (elastic) and irreversible effect (plastic).

Some other noteworthy work in thermodynamic analysis includes the work of McNichols and Cory [207] who treated the thermodynamics of Nitinol from a viewpoint of force-length-temperature state measurements. They predicted the cyclic path of Nitinol using a set of equations of thermodynamic state variables. Wollants et al. [208] not only gave comprehensive overview on the equilibrium thermodynamics

CHAPTER 2. Literature Review

of both thermally- and stress-induced martensitic transformation, but also evaluated the earlier concepts of frictional work and stored elastic energy. A one-dimensional thermodynamics and statistical thermodynamics model of pseudoelastic hysteresis loop was developed by Müller and Seelecke [209]. Their analytical model simulated the stress-induced martensitic transformation and that of reverse transformation, as well as the formation of predominant twins in the martensite phase (i.e. M_+ and M_-) with respect to the dynamism of collective lattice cells.

While it leads to an overall thermomechanical sketch of SME, the theory of micromechanics of defects in solids, and the foundation of solid mechanics offer clear description on the role of internal stress field and its relation to the production of elastic strain energy. In 1988, Patoor et al. [210] set forth a formulation of transformation plasticity describing the thermomechanical characteristic of SMAs. There are two kinds of transformation plasticity: i) Pure Transformation Plasticity (PTP); and ii) Coupled Transformation Plasticity (CTP). A thermoelastic phenomenon pertaining to SME and PE had been categorized under PTP because of their nature of martensite plate growth. It produces far less degree of internal stresses smaller than the yield point of the two phases. With elaborated work on the transformation plasticity, Berveiller et al. [98] attributed the development of internal stress and an associated stored energy to the formation of three main incompatibilities: i) mechanism of variant formation; ii) interaction of martensite plates with the microstructure of the austenite; and iii) interactions inside the martensite itself. In 1991 Patoor et al. [99] further conceptualized their micromechanics analysis of internal stress effect in the shape memory characteristics. They showed that the beginning of martensitic transformation (i.e. M_s -temperature) is affected by the internal stress associated with defects.

2.4 Thermodynamic and Macromechanical Analysis

In the area of macromechanical analysis, Stalmans et al. [61] applied the modified Clausius-Clapeyron equation based on a concept of stress dependence of transformation temperatures to approximate the amount of transformation strain. De Araújo et al. [53] attempted to put together the works of Patoor et al. [99] and Nomura et al. [50] to derive a model capable of estimating internal stress. Ingenuity displayed in macromechanical and thermodynamic analysis has led researchers to clarify some important aspects of the development mechanism of TWME. In a word, it has been articulated a belief to put emphasis on the macromechanical correlation between plastic strain/locally stabilized martensite and the magnitude of TWME.

What remains unsolved in the mystery of TWME, however, continues to attract researchers' interest including the present author. With this in mind, the present research has been dedicated to provide further quantitative and qualitative information on the two-way shape recovery characteristics in NiTi alloy.

CHAPTER 3

Experimental Setup and Procedures

This chapter begins with detailed description of the experimental setup. The description includes as-annealed NiTi sample preparation, the Instron microforce testing system and differential scanning calorimetry used to obtain experimental results during training and after training, respectively.

The NiTi SMA thin wire applied with uniaxial thermomechanical tests were performed using an Instron-type microforce testing system. The amount of shape recovery generated in SATWME and TWME were monitored real-time by recording the specimen's length change due to respective heating and cooling cycles. Each of the thermal cycles was programmed to perform repeated process that may consist of ramping up/down to a target temperature with specified ramping rate, and holding temperature at the start and end of every forward/reverse transformations.

A simplified flow diagram of the main experimental procedures is shown in Figure 3.1. In brief, the procedure begins with heat treatment of as-received NiTi wire, annealed at specified temperature and duration to remove any dislocation debris left behind from the fabrication process. Following the annealing process, the as-annealed wires were isothermally loaded, unloaded and reloaded in tension to undergo martensite deformation. Deformed specimens were thermally cycled under constraint

3.1 Sample Preparation

Figure 3.1 Experimental setup: main procedures.

to undergo training necessary for a development of TWME. All the mechanical loading and thermal cycling processes were carried out by using the Instron-type microforce testing system equipped with components: upper grip and pull-rod mounted onto a motor-driven longitudinal actuator, lower grip and pull-rod mounted on a load cell, and enclosed thermal chamber. The Instron microforce system was chosen literally for its small force detection capabilities. TA Instruments MDSC 2920 was used for the DSC measurements, providing useful thermodynamic data of the post-trained specimens.

3.1 Sample Preparation

The commercially available near equiatomic NiTi alloys produced in straight wire form with 0.508 and 0.185mm in diameter were used throughout in this research. Both wires were obtained from Nitinol Devices and Components of USA. The

CHAPTER 3. Experimental Setup and Procedures

specimens of approximately 110 and 75mm in length were cut from the as-received bulk items (i.e. wire diameter = 0.508 and 0.185mm, respectively) and both given with heat treatment at 580°C for 30min, followed by air-cooling to room temperature. To accommodate the annealing process, two different types of furnaces were considered initially: the one with open-air furnace (BRF14/5-2416 from Elite Thermal Systems Limited, equipped with EURO THERM temperature controller) capable of reaching as high temperature as 1200°C; and the other with argon gas furnace (R40/250/12-C6 from Nabertherm, equipped with a digital surface thermometer HFT-

Figure 3.2 Elite thermal systems open-air furnace: (a) door closed; and (b) enlarged view of furnace (door open).

Figure 3.3 Nabertherm argon gas furnace.

3.1 Sample Preparation

70 from ANRITU METER Co. Ltd.) that minimizes the oxidization effect during annealing. The overall setup and configuration of these furnaces are shown in Figures 3.2 and 3.3.

As for the case of open-air furnace (Figure 3.2), the annealing temperature and duration was set externally by programming the target temperature of the furnace. Owing much to the design configuration of the heating elements that are mounted onto the two sides of insulated wall, distribution of the temperature inside the furnace was found to vary (typically 20°C). To avoid inconsistency in sample preparation, the annealing temperature was monitored by means of placing an external thermocouple in direct contact with a specimen. The thermocouple measured the specimen's temperature not the surroundings. The duration of annealing process was counted immediately after the stabilization of thermocouple's temperature. In this way, the specimen was given the proper and consistent heat treatment prior to thermomechanical tests. Similar approach was taken for the case of argon gas furnace (Figure 3.3) that the annealing temperature was monitored using a digital surface thermometer, which was situated in direct contact with the specimen.

The as-annealed specimens prepared via two different furnaces were compared in light of DSC measurements. The results are shown in Appendix A. It can be seen that the DSC endothermic and exothermic curves projected almost the same thermodynamic features regardless of the two furnaces used (cf. Figure A.1 and A.2). Thus, we adopted the open-air furnace heat treatment method because of its ease of sample preparation.

3.2 Instron-type Microforce Testing System

An Instron-type microforce testing system was arranged to suit the isothermal

CHAPTER 3. Experimental Setup and Procedures

martensite deformation and constrained thermal cycling experiments, as shown in Figure 3.4. The tensile machine (8800 systems equipped with Series 3119 mini environmental chamber) is linked to the desktop PC and to the EUROTHERM temperature controller. In effect, the former device controls the mechanical longitudinal movement of the actuator, whereas the latter device controls the rise and fall of temperature inside the chamber with operating range: $-70 \sim 250^{\circ}\text{C}$ [89].

The specimen is heated by means of convection. A compressed hot air heated up by a heater is sprayed through one end of the hose, which is directly connected to the chamber. The cooling process is also carried out in similar manner that a compressed cool air, which is fed from the liquid nitrogen tank, is sprayed to the specimen. To ensure accuracy in recording the real-time temperature changes of a specimen, a thermocouple (EUROTHERM Q488-0C01) is placed in direct contact with the

Figure 3.4 Experimental apparatus: Instron Microforce Testing System.

3.2 Instron-type Microforce Testing System

specimen, as shown in Figure 3.5(a). Also, as can be seen from the figure, the tensile machine consists of an upper grip connected to the actuator at its top end and a lower grip connected to the load cell (i.e. 500N load cell is used in this arrangement) at its bottom end. In this apparatus arrangement, both grips were pneumatically driven so as to provide firm grip especially for the thicker wire (with diameter = 0.508mm). For the thinner wire (with diameter = 0.185mm) experiment, however, the tensile machine consisted of a customized grips and 50N load cell supplied by Instron. The experimental setup using such grips and 50N load cell is shown in Figure 3.5(b). The use of customized grips not only ensured no severe clamping damage to be imposed onto the specimen (i.e. clamping force adjustments were made by the mechanical fastening) but also suppressed the effect of thermal expansion to be minimum¹. The purpose of using lower ranged load cell for the case of thinner wire is due to its small cross-section area, i.e. small change in force causes large stress to be exerted. Thus, the use of 50N load cell is more appropriate for detecting this small change accurately. The 50 and 500N load cell provided accuracy of ± 0.05 and $\pm 0.1\%$, respectively (*see* Appendix B).

Prior to testing, displacement of the specimen (i.e. between two ends of the grips) was measured by a Mitsutoyo digital caliper (model 500-181) with accuracy of $\pm 0.02\text{mm}$. The gauge length was set at 55 and 60mm for the 0.185 and 0.508mm wire, respectively. All the loading, unloading and reloading processes applied for full or partial transformation were performed at a strain rate of $1 \times 10^{-4} \text{s}^{-1}$. This rate is considered sufficiently low to circumvent the strain rate effect on the martensite deformation characteristics [36, 211, 212]. The stress level reached upon completion of reloading process in a fully martensitic state was set to be the constrained stress (i.e.

¹ The thermal expansion coefficient for the 50 and 500N load cell fixture arrangement was measured to be about $18 \times 10^{-6}/^\circ\text{C}$ and $56 \times 10^{-6}/^\circ\text{C}$, respectively (*see* Appendix C).

CHAPTER 3. Experimental Setup and Procedures

Figure 3.5 Enlarged view and schematic of Instron-type tensile machine: (a) arranged with 500N load cell; and (b) arranged with 50N load cell (partly cross-sectioned).

externally applied stress was kept constant during thermal cycling). Sampling rate was set at two data points/sec, i.e. equivalent to 2Hz. When the testing system was set to run the thermomechanical experiment, dynamic data of force, displacement and temperature with respect to time elapsed were recorded and stored into the PC in Microsoft® Excel® format.

3.3 Differential Scanning Calorimetry Measurement

For the differential scanning calorimetry (DSC) measurement, a MDSC of type 2920 from TA Instruments was used. All the thermal properties of pre- and post-trained specimens were determined by this measurement method. For the preparation of calorimetric measurements, the specimens were carefully cut and polished to remove any oxidized layers. The masses were approximately 10mg for a wire with diameter 0.508mm. For a thinner wire, however, masses were reduced to 5mg approximately

3.3 Differential Scanning Calorimetry Measurement

due to its total sample weight (i.e. with 55mm gauge length, the total sample weight was only about 9mg).

The measurements were carried out with following settings unless otherwise stated: initiated by equilibrating temperature to 0°C followed by heating to 150°C, kept isothermal for 5min to obtain thermal equilibrium, then cooled down to 0°C, and kept isothermal for 5min again. This marks the end of 1st cycle and repeated if necessary to obtain multiple complete cycles. All heating and cooling rates were set at 5°C/min under atmospheric pressure. Helium was used for the purge gas.

3.4 Experimental Procedures

The thermomechanical experiments conducted in this research were divided broadly into three test conditions: Test (1) Fixed pre-strain with variable constrained stress; Test (2) Fixed constrained stress with variable pre-strain; and Test (3) Fixed pre-strain and constrained stress with increased number of cycles. The stress-strain-temperature and thermal cycling settings applied in these test conditions are summarized in Table 3.1. As seen in Table 3.1, each of the tests was divided further into two parts in terms of size and thermal cycling conditions: namely (a) Wire diameter with 0.508mm, full transformation; and (b) Wire diameter with 0.185mm, partial transformation. At this point, the effect of specimen's wire diameter on the shape recovery characteristic was not a major topic of discussion here (as will be shown later, the larger SATWME was generated for the thinner wire likely due to its stronger texture formations): the effect of texture formation on the shape recovery characteristics has been well-documented in [37, 154-157]. Nonetheless, a comprehensive discussion based on rich experimental analysis of two-way shape memory behavior due to partial transformation has been scarcely reported to date. Thus, it is deemed worthy of

CHAPTER 3. Experimental Setup and Procedures

further investigation to study the effect of full/partial transformation on the SATWME and the subsequent development of TWME.

Test conditions Variables	(1) Fixed pre-strain with variable constrained stress		(2) Fixed constrained stress with variable pre-strain		(3) Fixed pre-strain and constrained stress with increased no. of cycles	
	(a) Wire dia. = 0.508mm	(b) Wire dia. = 0.185mm	(a) Wire dia. = 0.508mm	(b) Wire dia. = 0.185mm	(a) Wire dia. = 0.508mm	(b) Wire dia. = 0.185mm
Pre-strain	8%	4%	3 ~ 18%	4 ~ 23%	8%	4%
Constrained stress	20 ~ 400MPa	50, 200, 350MPa	50, 200, 400MPa	200MPa	50, 200, 400MPa	200MPa
No. of training cycles (N)	1	1 + stress-free cycle	1	1 + stress-free cycle	4	4 + stress-free cycle
Thermal cycling (Full/Partial transformation)	Full	Partial	Full	Partial	Full	Partial

Table 3.1 Experimental parameter settings for the three major test conditions (1)-(3) considered.

3.4.1 Stress-Strain-Temperature Settings

For the full transformation tests, firstly the magnitude of constrained stress was treated as major variables, while fixing the pre-strain at 8% (Test (1a)). The evolution of the SATWME was observed by undergoing one *training cycle*. For the cases of 50, 200 and 400MPa, number of *training cycles* were repeated up to fourth cycle in order to observe their cyclic behavior (Test (3a)). Effectively, the cyclic shift of M_s -temperatures was extrapolated from the respective strain-temperature curves to estimate the development of internal stress. Another case of fixing the magnitude of constrained stress, while varying the pre-strain between 3 and 18% (Test (2a)) was also considered. The results obtained in these three test conditions allowed one to examine if there is any deformation procedure independence exist in SATWME.

While partial transformation had been applied at the first heating process under constraint for the cases of Test (1b) and (2b), other cyclic conditions were considered for the case of Test (3b). This allowed one to clarify some of the views on such

3.4 Experimental Procedures

Figure 3.6 Schematic of stress-strain-temperature settings: (a) loading, unloading and reloading processes at room temperature, T_{RM} ; and (b) loading processes and subsequent thermal cycling processes illustrated in stress-temperature phase diagram.

microstructural mechanisms responsible for the SATWME and TWME as the rearrangement of dislocations and martensite variant reconfigurations.

Parallel to the presentation of Table 3.1, the stress-strain-temperature settings applied in the various thermomechanical tests are illustrated in Figure 3.6. First, martensite deformation under tension is performed at room temperature, T_{RM} , which is measured to be approximately 20°C (below M_f -temperature of the as-annealed specimen). The deformation is initiated by loading the specimen to a predetermined pre-strain, ϵ_{PS} , followed by unloading to zero stress. By doing so leaves some amount of residual strain, ϵ_{RS} . The pre-strained specimen is then reloaded to a predetermined constrained stress, σ_C , at which the stress has been held constant to proceed with training cycles.

Training cycles were initiated by heating the specimen to a specified target temperature, T_H . In line with Clausius-Clapeyron relation [20], which is partly shown as a stress-temperature phase diagram in Figure 3.6(b), T_H was raised to a higher temperature for the higher σ_C condition to ensure complete shape recovery. For heating, the ramping up rate was set at 2°C/min, which is considered relatively slow

CHAPTER 3. Experimental Setup and Procedures

speed to avoid the temperature fluctuation. After reaching T_H , temperature was kept isothermal for 5min to fully establish the completion of reverse transformation. For cooling, the ramping down rate was set at $1^\circ\text{C}/\text{min}$; due to the characteristic of proportional-integral-derivative (PID) control that it produced higher aliasing magnitude and frequency during cooling process than that of heating process. Besides the PID control, to reduce further the chance of getting fluctuation during heating and cooling process, the front end anti-aliasing filter frequency was adjusted from 1kHz (default value) to 100Hz. Upon reaching T_{RM} (or even lower temperature for some test conditions), temperature is again kept isothermal for 5min to fully establish the completion of forward transformation. This sets the end of first *routine cycle*². The subsequent heating/cooling processes were repeated up to 4 training cycles for Test (3) conditions.

For the partial transformation, however, T_H was set between A_s and A_f temperatures during 1st heating (*see* Figure 3.8(a)). Once the T_H is reached, the cooling process immediately followed to bring the temperature back to below M_f . Subsequent to the partial reverse transformation is the full reverse transformation in the next heating.

3.4.2 Interpretation of Strain-Temperature Curve (full trans.)

As briefly described in Section 1.3, the magnitude of SATWME and TWME will be interpreted from the cooling-heating path generated in the respective strain-temperature curves. However, to elaborate it further on the interpretation of SATWME, its first cooling path will be derived from the 1st *routine cycle* whereas its first heating path will be derived from the 2nd *routine cycle* to establish the strain-

² See Figure 3.7(a).

3.4 Experimental Procedures

Figure 3.7 Interpretation of strain-temperature curve: (a) from routine cycle point of view, 1st and 2nd routine cycle comprised of 1st heating/cooling and 2nd heating/cooling, respectively; and (b) from training cycle point of view, 1st and Nth training cycle comprised of 1st cooling/2nd heating and 2nd cooling/3rd heating, respectively.

temperature curve of the 1st training cycle, as shown in Figure 3.7.

The complication arises from the fact that the specimen is in fully martensitic state at room temperature, and therefore the entire thermal cycling process can only be conducted at first by heating followed by cooling. As shown in Figure 3.7(b), the symbols ϵ_{MA} , ϵ_{RS} , ϵ_{TR} , ϵ_{SATW} , and ϵ_{IR} represents the martensitic strain, residual strain, transformation strain, stress-assisted two-way memory strain, and irrecoverable strain generated during 1st training cycle, respectively. It should be mentioned that the magnitude of ϵ_{MA} is considered as total strain deformation progressed in the course of martensitic transformation under constrained thermal cycling. Meanwhile, those symbols with (N) represent their strain values obtained at Nth training cycle. Obviously, the magnitude of ϵ_{SATW} was analyzed for the development of SATWME.

3.4.3 Interpretation of Strain-Temperature Curve (partial trans.)

The influence of partial transformation on the SATWME and TWME was monitored

CHAPTER 3. Experimental Setup and Procedures

by undergoing one training cycle followed by a stress-free cycle of cooling and heating. Obviously, this training condition directly corresponds to those of Test (1b) and (2b) listed in Table 3.1. In these test conditions, the partial transformation was imposed on the 1st heating.

Based on the partial reverse transformation results [64, 65] and model predictions [78, 213-215], the trace of partial transformation loops was expected to follow the full transformation loop upon 1st cooling, as shown in Figure 3.8(a). The degree of partial transformation was controlled by adjusting T_H , by which generates the partially transformed strain, ε_{PT} , and non-transformed strain as in retained martensite, ε_{RM} . The fully transformed strain is represented by ε_{FT} . In this regard, the amount of retained martensite (%RM) was estimated by the following relation: $\%RM = (\varepsilon_{RM} / \varepsilon_{FT}) \times 100\%$. A comparable approach was taken for the case of Test (3b) except that the partial transformation was not necessarily imposed on the 1st heating but on the next successive heating paths.

The transformation properties of the specimen due to partial transformation will

Figure 3.8 Interpretation of strain-temperature curve generated during: (a) 1st heating and cooling under a constant stress; and (b) 2nd heating under a constant stress, followed by stress-free 2nd cooling and 3rd heating via unloading.

3.4 Experimental Procedures

be studied by observing the macroscopic changes appeared in the relevant strain-temperature curves, as shown in Figure 3.8(b). With reference to the past literatures reported [68, 69, 71, 76, 77], it is predicted that the two-step reverse transformation would appear in the next full transformation due to single interruption. In this two-step transformation, we have taken novel approach to measure each of the recovery strains separately and given comparison with previously measured ε_{PT} and ε_{RM} . As will be shown later in Chapter 7, this macromechanical approach was particularly useful in evaluating the accommodation process of two distinct types of martensite variants (i.e. stress-assisted and retained detwinned/reoriented variants) and its aftermath on SATWME and TWME. From Figure 3.8(b), the magnitude of recovery strain in the first-half of reverse transformation, ε_{R1} , was measured between A_s' and A_f' temperatures. Likewise the magnitude of recovery strain in the second-half of reverse transformation, ε_{R2} , was measured between A_s and A_f temperatures.

In general, the transformation temperatures were determined by using a slope line extension method, drawing two tangential lines along the strain-temperature curve. The magnitude of two-way memory strain, ε_{TW} , appeared after unloading and stress-free 2nd cooling/3rd heating was analyzed for the development of TWME.

CHAPTER 4

Full Transformation and the Shape Recovery Characteristics

The mechanism of shape memory effect (SME) reviewed in Chapters 1 and 2 enabled us to outline some of the microscopic and macroscopic factors that are responsible for the amount of shape recovery. Recalling that the shape memorized by SME is that of high temperature austenite phase and is often called one-way SME. Meanwhile, when a shape memory material is deformed beyond its recoverable strain limit in a martensitic state, the shape recovery becomes incomplete and produces irrecoverable strain upon heating. However, owing much to this irrecoverable strain, the subsequent cooling causes spontaneous shape recovery called two-way memory effect (TWME). In this respect, TWME is obtained only after undergoing thermomechanical treatment. In one aspect of such treatment, where the specimen is thermally cycled under constant stress (i.e. constrained stress), results in the development of stress-assisted two-way memory effect (SATWME).

SATWME is comparable to TWME except that during cooling process, the nucleation and growth of martensites are preferentially oriented by the constrained stress producing large transformation strains due to stress-assisted martensite (SAM). During subsequent heating, SAM reverse transforms into austenite and the sample

CHAPTER 4. Full Transformation and the Shape Recovery Characteristics

recover back to its original shape.

Although much dedicated work has been conducted on the evolution of SATWME and TWME, the definitive thermomechanical correlation between these memory effects, of particular issues concerning the generation of maximum memory effect is still unclear, and thus deserves further investigation. Highlighted by this need, a number of thermomechanical test conditions were considered (cf. Table 3.1) and conducted in this chapter.

This chapter will begin by considering the characteristics of SATWME under full transformation condition. In Section 4.1, fixed pre-strain condition (Test (1a)) will be considered to examine the stress dependence on the transformation properties that are manifested in the strain-temperature and stress-temperature curves. Reliability and reproducibility of the experimental results are presented in Appendix D. After having established the optimum condition for generating maximum SATWME as a function of constrained stress, the shape recovery behavior of SATWME will then be further characterized by changing the magnitude of pre-strain, while fixing the magnitude of constrained stress (Test (2a)). The result will be presented and discussed in Section 4.2. A key observation in these tests will include martensite deformation procedure independence in achieving maximum SATWME, i.e. achieved by the direct application of pre-strain or by the cyclic shift of martensitic strain.

In Section 4.3, the cyclic shift of martensitic strain will be examined further by increasing the number of training cycle (Test (3a)). Meanwhile, the succession of strain-temperature curves produced from this cyclic test will be used to estimate the magnitude of internal stress developed during training via macromechanical approach [53]. Further remarks and an overall summary of the experimental/macromechanical results will be presented in Section 4.4.

CHAPTER 4. Full Transformation and the Shape Recovery Characteristics

4.1 Test (1a): Characteristics of SATWME in Fixed Pre-strain Condition

4.1.1 Stress-Strain Analysis

The stress-strain relationship obtained under monotonic tension in a fully martensitic state describes detwinned martensite and dislocation formation via increased loading.

Figure 4.1 shows the stress-strain curve obtained from the as-annealed NiTi wire with diameter 0.508mm, tensioned to 8% pre-strain. After unloading to reach zero stress, the specimens were reloaded to reach various constrained stress levels namely, 20, 50, 100, 200, 300, and 400MPa. The 20, 100 and 400MPa levels are indicated by the arrows in the figure. It can be seen from the stress-strain profile that the first yield, σ_y , occurred at about 130MPa, and the *stress plateau* progressed until about 4.3% strain showing clear indication of partial detwinning process. The width of stress plateau was measured to be about 3%. Following the emergence of stress

Figure 4.1 Stress-strain curve obtained at room temperature for as-annealed NiTi wire with diameter = 0.508mm.

4.1 Test (1a): Characteristics of SATWME in Fixed Pre-strain Condition

plateau, abrupt nonlinear stress increase is evident with increasing magnitude of strain deformation. This nonlinear stress increase implies the occurrence of a further detwinning process, where the generation of dislocation is highly expected [29-31, 216, 217]. The role of dislocation in the shape recovery characteristics will be discussed in light of strain-temperature analysis following this section.

4.1.2 Strain-Temperature Analysis

Figure 4.2 shows the development of SATWME in its first training cycle. The as-annealed specimen was subjected to a fixed 8% pre-strain and various degrees of constrained stress ranged between 20 to 400MPa. It is seen from Figure 4.2 that the SATWME comprised of the transformation strain, ϵ_{TR} , the stress-assisted two-way memory strain, ϵ_{SATW} , and the gap representing irrecoverable strain, ϵ_{IR} . Apart from

Figure 4.2 The characteristics of SATWME under various constrained stress conditions.

CHAPTER 4. Full Transformation and the Shape Recovery Characteristics

these strains, the magnitude of residual strain, ε_{RS} , and martensitic strain, ε_{MA} , measured from zero strain level to the respective initiation and termination of 1st cooling rises with increasing constrained stress. Following the trend of ε_{RS} and ε_{MA} , the transformation temperatures M_s , M_f , A_s and A_f , as determined by the intersection of two tangential lines drawn along the strain-temperature curve, increases with increasing constrained stress. This is closely in line with the Clausius-Clapeyron relationship; as the applied external stress increases so do the transformation temperatures [25, 42].

The characteristics of ε_{SATW} and ε_{IR} generated during the first training cycle as a function of constrained stress are summarized in Figure 4.3. It becomes apparent that the value of ε_{SATW} increases with increasing constrained stress to a maximum of 4.2% at 200MPa. Further increase beyond this stress level resulted in a sharp decline to reach 2.4% at 400MPa. On the contrary, the value of ε_{IR} increases abruptly from almost nil to 5.3% with increasing stress from 20 to 400MPa, respectively. It has been observed [21, 61] that ε_{IR} is introduced due to either true plastic deformation (i.e. dislocations) or locally stabilized martensite retained above A_f . However, considering that there is no evidence of two-step transformation in Figure 4.2 when compared with previous results [61], ε_{IR} generates due to introduction of dislocations. Thus, the trend observed in ε_{SATW} and ε_{IR} is comparable with the TWME that having excessive dislocations will lead to a decrease in two-way memory strain [28, 33, 36, 38].

The characteristics of ε_{RS} , ε_{MA} , and ε_{TR} as a function of constrained stress are summarized in Figure 4.4. The value of ε_{RS} increased almost linearly from 2.7 to 8.7% with a corresponding increase in constrained stress from 20 to 400MPa. A

4.1 Test (1a): Characteristics of SATWME in Fixed Pre-strain Condition

Figure 4.3 Influence of constrained stress on the magnitudes of stress-assisted two-way memory strain and irrecoverable strain generated during the first training cycle.

Figure 4.4 Influence of constrained stress on the magnitudes of residual strain, martensitic strain and transformation strain generated during the first training cycle.

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comparable characteristic is manifested in ε_{MA} that its value increased from 5 to 16.4%.

With reference to Figure 4.1, if the specimen is reloaded to a high stress level such as 400MPa, the strain value surpasses the previously determined pre-strain 8%. The transformation strain, ε_{TR} , generated in the cooling part of training cycle will be assisted by the constrained stress. In other words, the value of ε_{TR} increases with increasing constrained stress and the value of ε_{MA} amplifies as a result. It is known that constrained cycling leads to the growth of stress-assisted martensite (SAM) in expense of other martensite variants [24, 34]. In this regard, the growth of SAM is said to be weak under low constrained stress condition, resulting in a small change of ε_{MA} from the applied 8% pre-strain. In addition to this characteristic, it is noteworthy to mention that there is a clear transition point appeared on the ε_{MA} at 200MPa, as indicated by the downward arrow in Figure 4.4. Given the fact that the excessive amount of ε_{MA} would result in poor ε_{SATW} (accompanied by the drastic increase of ε_{IR} especially after the transition point), the magnitude of ε_{MA} can be utilized as an experimental parameter. This determines the amount of shape recovery, as is equivalent to a magnitude of pre-strain determines the TWME [28].

As discovered from Figures 4.2 and 4.3, there is clear a tradeoff between having complete SATWME at lower constrained stress condition and attaining high ε_{SATW} but having incomplete SATWME at higher constrained stress condition. In the latter case the generation of ε_{IR} is unavoidable.

4.1.3 Stress-Temperature Analysis

The stress dependence on the transformation temperatures M_s , M_f , A_s , and A_f were

4.1 Test (1a): Characteristics of SATWME in Fixed Pre-strain Condition

characterized by plotting the stress-temperature phase diagram, as determined from the strain-temperature curves (Figure 4.2). The results are shown in Figure 4.5. As far as the Clausius-Clapeyron relationship verifies (cf. equation (1.1)), the change in applied stress, $d\sigma$, and the change in transformation temperature, dT , which are reflected respectively on the y-axis and x-axis of the figure, should obey linear relationship. It can be seen that this relationship is proven to be particularly true for the forward transformation temperatures (M_s and M_f). However, the reverse transformation temperatures (A_s and A_f) neither appeared to project a strict linear relation nor aligned parallel to each other.

The above result is likely attributed to two facts: first, because transformation temperatures were determined by intersecting the two tangential lines drawn along the strain-temperature curve, difficulty arose when the shape of the curve became severely distorted. This refers to the cases of 200, 300, and 400MPa. The distortion of the curve was somewhat reflected by the corresponding nonlinear portion of the

Figure 4.5 Stress-temperature curve of as-annealed NiTi specimen subjected to one training cycle.

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reverse transformation lines shown in Figure 4.5. Second, referring back to the strain-temperature curve (Figures 4.2 and 4.4), it is noticed that the value of ε_{MA} exceeds the value of initial 8% pre-strain after 100MPa constrained stress. This important experimental evidence implies that owing to the increase in ε_{MA} the extent of martensite deformation progresses further to increase the density of dislocations in the 1st cooling. It requires extra heating to complete the reverse transformation in the 2nd heating, as observed.

Based on the stress-temperature curve defined in Figure 4.5, the stress dependence on the temperature intervals ΔM ($= M_s - M_f$), ΔA ($= A_f - A_s$), and hysteresis ($= (A_s + A_f)/2 - (M_s + M_f)/2$) has been investigated. The results are shown in Figure 4.6. Evidently, the increase in stress from 20 to 300MPa causes the value of ΔM to be increased by 9°C approximately, and a further increase to 400MPa causes noticeable drop by about 5°C. On the contrary, the value of ΔA projected a steady

Figure 4.6 Influence of constrained stress on the magnitudes of transformation temperature intervals (ΔM , ΔA) and hysteresis width obtained during the first training cycle.

4.1 Test (1a): Characteristics of SATWME in Fixed Pre-strain Condition

increase to about 50°C with increasing stress to 400MPa. It is also observed that the value of ΔA is inclined to be higher than that of ΔM and besides, the difference between these intervals became far apart as the magnitude of constrained stress increases. As a consequence of the increased transformation temperature intervals (ΔM and ΔA), the hysteresis widens, frictional resistance to interfacial motion increases and dissipation of stored elastic energy increases. In order to overcome these non-chemical energy barriers arising from the elastic energy and frictional resistance, increased chemical energy is required to initiate and complete the reverse transformation [24]. This is reflected by the increase in A_s -temperature and by the prolonged heating to reach A_f -temperature.

4.2 Test (2a): Characteristics of SATWME in Fixed Constrained Stress Condition

4.2.1 Stress-Strain Analysis

In view of the fact that maximum SATWME was observed at 200MPa in Test (1a), now our interest lies in characterizing its shape recovery behavior when subjected to variable pre-strains with fixed constrained stress of 200MPa. Nonetheless, two other lower/higher constrained stress conditions were also considered (i.e. 50 and 400MPa) in the meantime as to capture the overall picture of SATWME characteristics. In these 50, 200, and 400MPa constrained stress conditions, the pre-strains were set between 3 and 18% to bring about the Lüders-like deformation [31, 218-220] and massive introduction of dislocations [32, 33].

Figure 4.7(a) shows the examples of stress-strain curves subjected to 3, 8, and 18% pre-strain, unloaded to zero stress, followed by reloading to 50, 200, and 400MPa, respectively. Note that the stress-strain curves generated under other

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Figure 4.7 Examples of stress-strain curves (as-annealed NiTi with diameter 0.508mm) subjected to various degrees of pre-strain and constrained stress: (a) 3% pre-strain and 50MPa, 8% pre-strain and 200MPa, 18% pre-strain and 400MPa; and (b) 3 – 18% pre-strains and 400MPa.

conditions of pre-strain and constrained stress are omitted here for clarity. To supplement the stress-strain curves shown in Figure 4.7(a), additional curves are produced for the case of the specimen subjected to 3 – 18% pre-strains and 400MPa constrained stress, as shown in Figure 4.7(b). As observed in Section 4.1.1, the abrupt increase of stress occurred after the Lüders-like deformation identified by a stress plateau. The linear response of stress-strain curve enters into nonlinear response after about 13% strain deformation, showing the second plastic yield stress, σ_y' , at about 630MPa. These observations are in good agreement with previous studies [31, 33].

4.2.2 Strain-Temperature Analysis

A single training cycle was performed for those specimens that had undergone various magnitudes of pre-strain namely 3, 4, 8, 10, 13 and 18%, and constrained stress of 50, 200 and 400MPa. Figure 4.8(a), (b) and (c) show the SATWME generated for the cases of 50, 200 and 400MPa constrained stress, respectively.

For the case of 50MPa shown in Figure 4.8(a), the specimen deformed in the stress plateau zone (3, 4% pre-strain) projected an insignificant strain recovery with

4.2 Test (2a): Characteristics of SATWME in Fixed Constrained Stress Condition

Figure 4.8 SATWME developed in the first training cycle, subjected to various magnitudes of pre-strain and: (a) 50MPa constrained stress; (b) 200MPa constrained stress; and (c) 400MPa constrained stress.

conspicuous shallow inclination of strain-temperature curve, requiring extra heating and cooling in their respective phase transformations. Further pre-strain to 8, 10, and 13% enters into further detwinning zone, where density of dislocations are produced in the microstructure [29-32, 221]. This results in the incomplete SATWME loop. The incomplete loop is evidenced by the gap, which is equivalent of an irrecoverable strain, ε_{IR} . The martensitic strain, ε_{MA} , and residual strain, ε_{RS} , rises with increasing magnitude of pre-strain. Under 200MPa constrained stress condition shown in Figure 4.8(b), however, reveals no significant change in these strain levels until the pre-strain had increased to 18%. Similar result is obtained for the case of 400Ma, as shown in Figure 4.8(c).

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The combined effect of pre-strain and constrained stress on the stress-assisted two-way memory strain, ε_{SATW} , measured directly from Figures 4.8(a)-(c) is shown in Figure 4.9. It can be seen that the 50MPa curve is characterized by the drastic increase of ε_{SATW} until 8% pre-strain, followed by the gradual increase to a maximum of 4.2% at 13% pre-strain. Further increase in pre-strain resulted in the decline to about 3.8% at 18% pre-strain. The 200MPa curve is insensitive to the effect of pre-strain until 8% pre-strain though, it starts to increase to a maximum of 4.3% at 13% pre-strain and shows decline to reach about 3.8% at 18% pre-strain. The 400MPa curve, however, showed distinctive recovery behavior that the value of ε_{SATW} remained virtually the same until 10% pre-strain, whereas steady increase is observed thereafter until 18% pre-strain. Noticeably, the value of ε_{SATW} coincides at 18% pre-strain regardless of the magnitude of constrained stress applied. Although this was the observation made thus far in [222], it is noticed that, in further pursuit of SATWME the characteristic

Figure 4.9 Combined effect of pre-strain and constrained stress on the magnitude of stress-assisted two-way memory strain obtained during the first training cycle.

4.2 Test (2a): Characteristics of SATWME in Fixed Constrained Stress Condition

of ε_{SATW} is more accurately analyzed with respect to *total strain deformation*, as explained below.

The degree of total strain deformation is proposed to be defined either by the degree of pre-strain or martensitic strain, ε_{MA} , i.e. if the magnitude of pre-strain is greater than ε_{MA} , then pre-strain would be a predominant factor to set the degree of total strain deformation and vice versa. This argument can be supported by the experimental evidences (Figures 4.8 and 4.9). For the case of 50MPa, pre-strain is dominant over ε_{MA} such that the value of ε_{SATW} directly increases/decreases as a function of pre-strain. The opposite scenario holds true for the case of 400MPa, where ε_{MA} being dominant over pre-strain, i.e. the value of ε_{SATW} is found to be almost the same when subjected to 3–10% pre-strain, while witnessing the identical value of ε_{MA} in these pre-strain conditions. Evidently, increase in ε_{MA} is observed after 10% pre-strain and resulted in an increase of ε_{SATW} (note that ε_{MA} increases beyond the initial pre-strain magnitudes).

Based on the comparison approach adopted between pre-strain and ε_{MA} , the degree of total strain deformation has been quantified for the cases of 50, 200, and 400MPa constrained stress. The results are summarized in Table 4.1. As mentioned earlier, the summary produced herein confirms the tendency that the value of pre-strain is greater than that of ε_{MA} under low constrained stress, and this strain relation becomes the opposite with increasing constrained stress to 200MPa and even higher to 400MPa.

Now our interest lies in re-assessing the characteristic of ε_{SATW} as a function of total strain deformation coupled with 50, 200 and 400MPa constrained cycling. Again, these constrained stress levels were chosen for two reasons: i) 200MPa was found to

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Pre-strain (%)	50MPa		200MPa		400MPa	
	ε_{MA} (%)	Total strain deformation (%)	ε_{MA} (%)	Total strain deformation (%)	ε_{MA} (%)	Total strain deformation (%)
3	<i>3.4</i>	3.4	<i>10.1</i>	10.1	<i>16.9</i>	16.9
4	<i>4.2</i>	4.2	<i>9.7</i>	9.7	<i>16.6</i>	16.6
8	6.9	8.0	<i>10.6</i>	10.6	<i>16.6</i>	16.6
10	7.9	10.0	<i>10.8</i>	10.8	<i>17.1</i>	17.1
13	9.6	13.0	11.4	13.0	<i>18.6</i>	18.6
18	13.2	18.0	17.7	18.0	<i>22.6</i>	22.6

Table 4.1 Degree of *total strain deformation* defined via comparison of pre-strain and ε_{MA} measured in 1st cooling; the values highlighted in italic indicate ε_{MA} being dominant over pre-strain.

be optimum in generating maximum SATWME [45, 57, 161, 223], and ii) to investigate the shape recovery behavior under both lower and higher levels than the optimum stress magnitude. The reassessed results are shown in Figure 4.10. Compared with the previous results (Figure 4.9), there is a major discrepancy in the characteristic of 400MPa that the value of ε_{SATW} does not coincide with other two constrained stress conditions at 18% martensite deformation. However, it can be predicted from the decreasing trend in 50 and 200MPa that the value of ε_{SATW} is likely to coincide at around 20% deformation independently of constrained stress. In addition, 400MPa showed distinctive characteristic that, although it is not possible to determine the maximum value of ε_{SATW} in this observation, the maximum would be located at much higher deformation level compared to the cases of 50 and 200MPa. This phenomenon is comparable to the effect of cold-work on the SATWME [45, 55].

Measurements of the irrecoverable strain, ε_{IR} , and the transformation strain, ε_{TR} , generated during cooling of the first training cycle as a function of total strain deformation are shown in Figure 4.11 and 4.12, respectively. It is evident that the generation of ε_{IR} is virtually negligible for the case of 50MPa, which makes the strain

4.2 Test (2a): Characteristics of SATWME in Fixed Constrained Stress Condition

Figure 4.10 Influence of total strain deformation and constrained stress on the magnitude of stress-assisted two-way memory strain generated during the first training cycle.

characteristic of ε_{TR} almost the same as that of ε_{SATW} . This implies that the amount of dislocations introduced during constrained cycling is at minimum. For the cases of 200 and 400MPa, the value of ε_{TR} remain higher than that of corresponding ε_{SATW} and thereby causing the generation of ε_{IR} .

As has been observed in the previous test condition (Test (1a)), the results shown in Figure 4.12 also confirm the transformation strain characteristic that higher the external stress is applied, the greater is the ε_{TR} . In the 200MPa condition, there was noticeable decrease in ε_{IR} after about 10% deformation and this decreasing trend continues until reaching its minimum at 13%. Further deformation to 18% resulted in the increase of ε_{IR} . The 400MPa condition also exhibited a clear decreasing trend of ε_{IR} with increasing deformation beyond 17%.

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Figure 4.11 Influence of total strain deformation and constrained stress on the magnitude of irrecoverable strain generated during the first training cycle.

Figure 4.12 Influence of total strain deformation and constrained stress on the magnitude of transformation strain generated during the first training cycle.

4.2 Test (2a): Characteristics of SATWME in Fixed Constrained Stress Condition

4.2.3 Temperature Intervals Analysis

The effect of total strain deformation coupled with 50, 200 and 400MPa constrained cycling on the transformation temperature intervals are shown in Figure 4.13(a), (b) and (c), respectively. In the case of 50MPa, the value of ΔM is at maximum at 3 to 4% deformation. This was reflected by the shallow inclination of the strain-temperature curve (Figure 4.8(a)). Increasing deformation to 10% in this constraint condition resulted in the decrease of ΔM to its minimum and further deformation showed slight increase to reach 3°C at 18% deformation. In essence, the reduction in ΔM indicates low stored elastic strain energy [24], and due to this effect requires more heating to start the reverse transformation.

The trend in ΔA is consistent with the ΔM and hysteresis growth. As a consequence of stored elastic strain energy dissipation (decrease in ΔM with increasing deformation to 10%), less elastic strain energy would be available to assist the reverse transformation. This will require larger chemical energy (i.e. extra heating) to initiate and complete the reverse transformation, hence the increase of ΔA . It follows that dislocation density due to constrained cycling increases to its maximum at 10% deformation (reflected by ε_{IR} in Figure 4.11). The frictional resistance to interfacial motion increases and hysteresis widens as a result. It is also noticed that the hysteresis width observed under 50MPa is comparable to the ones under stress-free condition [28].

For the case of 200MPa, the temperature intervals ΔM and ΔA both decreased to their minimum at 13% deformation reaching approximately 2.8 and 12.4°C, respectively. Noticeably, the maximum SATWME was achieved at this deformation level where the value of ε_{IR} is found to be minimum. Further increase in deformation

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Figure 4.13 Characteristic of temperature intervals as a function of total strain deformation and constrained cycling conditions: (a) 50MPa constrained stress; (b) 200MPa constrained stress; and (c) 400MPa constrained stress.

to 18% resulted in the slight increase of ΔM and ΔA . The hysteresis width, on the other hand, showed gradual decrease from 48 to 44°C in the course of reaching about 11% and further deformation to 18%.

For the case of 400MPa, unlike other two cases examined, each of the temperature intervals revealed distinctive features. ΔM decreased to its minimum at 18.6% deformation, followed by a sharp increase to reach about 10°C at 22.6% deformation. Whereas the value of ΔA showed continuous decreasing trend after about 17% deformation, the hysteresis width did not obey the trend of ΔA , but rather showed continuous increase to reach about 58°C at 18.6% deformation, followed by a

4.2 Test (2a): Characteristics of SATWME in Fixed Constrained Stress Condition

slight decline to reach 56°C at 22.6% deformation. The characteristics of temperature intervals induced by various magnitudes of total strain deformation and constrained stress will be further discussed in Section 4.3.2.

4.3 Test (3a): Cyclic Characteristics of SATWME

4.3.1 Strain-Temperature Analysis

Cyclic characteristics were observed when the as-annealed specimen was subjected to 8% pre-strain, constrained at 50, 200 and 400MPa, and thermally cycled at these stress levels for four complete training cycles. The strain-temperature curves produced under 50, 200, and 400MPa condition are shown in Figure 4.14(a), (b), and (c), respectively. Note, however, that only the part of 5th cycle is shown in the figures since the training cycle ended with cooling.

It is apparent that the changes in strain-temperature curve are more pronounced at higher constrained stress. As indicated by the closed arrow in the figures, the value of M_s -temperature, for instance, changes more abruptly under 400MPa constrained cycling. The progressive increase in M_s observed during training cycle is an indicative of development of internal stress [50, 53, 99]. In general belief, internal stress directs the orientation of martensite variants toward the direction of external stress and results in the development of TWME. From Figure 4.14, it is also observed that the A_s -temperature (indicated by the open arrow) progressively decreases for all the constraint conditions. Regardless of constraint conditions, the generation of irrecoverable strain, ε_{IR} , is inevitable at the initial cycle, but it progressively diminishes with increasing number of cycles. This observation of decrease in ε_{IR} due to cyclic effect can be attributed to the rearrangement of dislocation configuration

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Figure 4.14 Cyclic effect on the strain-temperature curves subjected to 8% pre-strain and thermal cycling under constraint: (a) 50MPa; (b) 200MPa; and (c) 400MPa.

formed by martensite deformation [148, 224]. The strain level in the martensite phase (i.e. ε_{MA}) and the austenite phase (i.e. ε_{RS}) tends to rise with increasing number of training cycles. This tendency is more pronounced for the 400MPa constrained cycling.

Figure 4.15 summarizes the characteristic of stress-assisted two-way memory strain, ε_{SATW} , directly measured from the strain temperature curves shown in Figure 4.14. It is apparent that drastic change in the value of ε_{SATW} occurred during the first two training cycles, which became more gradual upon further cycling to 4th cycle. Comparable cyclic effect is seen in the characteristic of ε_{IR} , as shown in Figure 4.16.

4.3 Test (3a): Cyclic Characteristics of SATWME

These phenomena can be explained from the viewpoint of a work hardening linked with the progress of martensite deformation.

The progressive rise of martensitic strain, ε_{MA} , due to repeated thermal cycling causes the extent of martensite deformation to be progressed further. It is evident that the value of ε_{MA} increases with increasing number of training cycles, as shown in Figure 4.17. The progress of martensite deformation introduces newly formed dislocations¹ and the existing dislocations will be rearranged by the thermal cycling. This will lead to a change in internal stress field [145, 148], as is evidenced by the change in M_s -temperature. The cyclic effect is eventually suppressed by the work hardening due to which dislocations may hardly move during thermal cycling. Thus, the changes in the value of ε_{SATW} , ε_{IR} , and M_s become gradual at the later cycle.

The role of dislocations in shape recovery characteristics can be elaborated further as follows. During the training cycles, a dislocation network has been developed that was most favorable to the internal stress field. This will in turn causes the martensite variants to be aligned in a preferential orientation [80, 81, 85, 181], making it possible to develop a SATWME in the current case. Based on these microstructural aspects and on the cyclically-induced propagation of deformation, it can be suggested that undergoing training cycle with high constrained stress of 400MPa produces high density of dislocations. The dislocations were, however, effective in producing preferentially oriented martensite, resulting in the increase of ε_{SATW} with increasing number of cycle (Figure 4.15). As will be explained in more detail later, the increase in the forward transformation temperature interval (ΔM) shows the sign of increase in elastic strain energy, which further signifies the increase

¹ With reference to the stress-strain curve shown in Figure 4.7, the value of ε_{MA} measured at the 1st cycle falls under the further detwinning zone in which the martensite reorientation will be accompanied by the generation of dislocations.

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Figure 4.15 Cyclic characteristic of stress-assisted two-way memory strain subjected to 50, 200, and 400MPa constrained stress.

Figure 4.16 Cyclic characteristic of irrecoverable strain subjected to 50, 200, and 400MPa constrained stress.

4.3 Test (3a): Cyclic Characteristics of SATWME

Figure 4.17 Cyclic characteristic of martensitic strain subjected to 50, 200, and 400MPa constrained stress.

in the volume fraction of martensite variants that are preferentially oriented to the external stress [24].

In contrast to the 400MPa condition, training under low constrained stress of 50MPa showed insignificant effect on ε_{SATW} . The value of ε_{SATW} merely showed an increase from 3.4 to 3.8% and it seems to have reached a maximum level already at the end of 4th cycle. The training under 200MPa also revealed insignificant change in ε_{SATW} , though the value of ε_{SATW} remained the highest (4.3%) amongst other two conditions. This phenomenon may arise from the fact that training under 200MPa made full utilization of the martensite reorientation capacity that leads to the establishment of a favorable internal stress field and aligned martensite variants.

The development of favorable internal stress field and its estimation will be further discussed in Section 4.4.

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4.3.2 Temperature Intervals Analysis

As observed in the previous section, an increase in constrained stress produces more severe plastic deformation (reflected by the value of ε_{IR}). The frictional barrier to phase boundary motion increases to widen the hysteresis. As shown in Figure 4.18, hysteresis width is observed to be the highest for the 400MPa. However, it is shown to decrease continuously with increasing number of cycles irrespective of constrained stress magnitudes. The result suggests that frictional resistance to interfacial motion is lowered by the elastic strain energy contributions.

In essence, elastic strain energy in SMA arises from two major contributions: i) elastic accommodation of transformational shape change where the buildup of elastic strain energy opposes further growth of martensite [95, 134, 199, 225], resulting in an increase of temperature interval ΔM ; and ii) plastic accommodation of shape change associated with the presence of internal stress fields in the material [99, 225]. The buildup of former contribution is assessed by the two evidences: firstly, the value of temperature interval ΔM rises with increasing number of cycles, as shown in Figure 4.19, indicating that more elastic strain energy is stored during the forward transformation; secondly, this stored elastic energy assists the reverse transformation whereby less heating is necessary to initiate the transformation, as is evidenced by the decreasing A_s -temperature (Figure 4.14). The buildup of latter contribution is reflected by the progressive increase of M_s -temperature with increasing number of cycles (Figure 4.14), and this will be further discussed in the next section.

Despite the observed decrease of both A_s and hysteresis width (i.e. internal work overcoming the frictional barriers opposing interfacial motion decreases), the duration of superheating, ΔA , increases for the cases of 50 and 200MPa with increasing number of cycles, as shown in Figure 4.20. This phenomenon is ascribed to the new

4.3 Test (3a): Cyclic Characteristics of SATWME

Figure 4.18 Cyclic characteristic of hysteresis width measured from the strain-temperature curves under constraint conditions of 50, 200, and 400MPa.

Figure 4.19 Cyclic characteristic of forward transformation temperature interval (ΔM) measured from the strain-temperature curves under constraint conditions of 50, 200, and 400MPa.

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Figure 4.20 Cyclic characteristic of reverse transformation temperature interval (ΔA) measured from the strain-temperature curves under constraint conditions of 50, 200, and 400MPa.

dislocations introduced by thermal cycling. As a general trend, it is known that dislocations are introduced when the specimen experiences two-way shape memory training [181, 226]. With continued thermal cycling, these dislocations tangles and the density increases [148, 149, 163]. Hence, these dislocations become the source of obstruction to the course of reverse transformation that leads to an increase of ΔA . However, the reason why the ΔA decreases for the case of 400MPa is because of its strong external force that the rearrangement of dislocations and martensite variant reconfigurations are enhanced.

4.4 Development of Internal Stress

Internal stress is a stress that remains in a material in the absence of applied external forces. The original cause of internal stress includes plastic deformation (e.g.

4.4 Development of Internal Stress

dislocations) and heat treatment (e.g. localized heat gradient introduced via welding process). Fundamentally, when solid materials are plastically deformed, the atoms that exist around dislocations are displaced from their perfect lattice sites [101, 227]. The resultant lattice distortion produces an internal stress field around the dislocations. In the case of edge dislocation, as illustrated in Figure 4.21, extra half-plane of atoms imposes region of compressive internal stress field above the slip plane: the region below is in tension. It has been suggested by many researchers [82, 83, 85-87, 179] that TWME originates from internal stress formations.

Figure 4.21 Illustration of internal stress field formed around edge dislocation [227].

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In the present research, any macroscopic change in M_s -temperature during cycling is connected to the development of internal stress. Apart from constrained thermal cycling technique, the development of internal stress has been corroborated by the decreasing trend of critical stress for inducing martensite in pseudoelastic cycling [143, 145, 146, 151, 186, 228-233]. As illustrated in Figure 4.22, the critical stress, σ_c , decreases to $\sigma_{c(N)}$ as the number of cycle progresses and the permanent strain, ε_p , generates due to slip deformation in the preceding cycle. The internal stress field formed by the slip deformation is believed to assist the nucleation of stress-induced martensite, and the critical stress thus decreases [143, 145, 146, 228, 232, 233].

From a thermodynamic viewpoint, the decrease in σ_c is thought to be equivalent to the increase of M_s caused by constrained thermal cycling. In brief, the changes in total Gibbs free energy due to thermomechanical forward $A \rightarrow M$ transformation process, defined as $\Delta G_{net}^{A \rightarrow M}$, in shape memory alloy can be analyzed thermodynamically [99]:

$$\Delta G_{net}^{A \rightarrow M} = [B(T - M_s)V_M] - \left[\int_V (\sigma_{ij}^0 + \sigma_{ij}^S) \varepsilon_{ij}^M dV + \frac{1}{2} \int_V \sigma_{ij}^M \varepsilon_{ij}^M dV \right] \quad (4.1)$$

where the terms inside the first and second square bracket represents the chemical and non-chemical component of the Gibbs free energy; B is a coefficient related to the chemical composition and the nature of transformation, T is the temperature, V_M and V are the transformed volume fraction of martensite and the volume of specimen, respectively, σ_{ij}^0 , σ_{ij}^S , and σ_{ij}^M are, respectively, the applied stress, the internal stress

Figure 4.22 Schematic example of pseudoelastic cyclic deformation.

developed by the presence of defects and the internal stress associated with the martensitic transformation, and ε_{ij}^M is the transformation strain.

From equation (4.1), it would be consistent to observe the reduction in $\Delta G_{net}^{A \rightarrow M}$ if M_s increases due to repeated thermal cycling under stress (i.e. requiring less thermodynamic energy to initiate the transformation). Likewise, repeated pseudoelastic cycling under constant temperature reduces the value of $\Delta G_{net}^{A \rightarrow M}$ due to the increase of σ_{ij}^S . This contributes to the lowering of σ_{ij}^O , since the internal stress field acts as a supplementary loading stress. The lowering of $\Delta G_{net}^{A \rightarrow M}$ due to abovementioned constant stress or temperature cycling can be verified by the schematic representation of free energy-temperature-pressure (G - T - P) diagram [208], which will be discussed in more detail in Chapter 6.

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The presence of accumulated internal stresses due to repeated pseudoelastic cycling was confirmed by the electron backscatter diffraction technique [234]. With reference to these microscopic observation and macromechanical formulation, it is reasonable to expect the development of internal stress via constrained thermal cycling.

In the case of constrained thermal cycling, the development of internal stress can be estimated by the modified Clausius-Clapeyron equation [53]:

$$\Delta\sigma_{INT}(\sigma_{EXT,N}) = \frac{\Delta\sigma_{EXT}}{\Delta M_s}(N) \cdot \Delta M_s(\sigma_{EXT,N}) \quad (4.2)$$

where $\Delta\sigma_{INT}(\sigma_{EXT,N})$ is the change in internal stress as a function of the external stress² σ_{EXT} and number of training cycles N , $\Delta\sigma_{EXT} / \Delta M_s(N)$ is the characteristic gradient extrapolated at every N^{th} cycle, and $\Delta M_s(\sigma_{EXT,N})$ is the change in M_s -temperature as a function of the global stress σ and number of training cycles N . Three external stresses were chosen in this analysis, namely 50, 200, and 400MPa³. In order to validate the applicability of equation (4.2), the stability of M_s during stress-free thermal cycling, which is measured by differential scanning calorimetry (DSC) method, and the relationship between M_s and external stress were examined. DSC result of 8% pre-strained specimen subjected to twenty stress-free thermal cycling is shown in Figure 4.23(a). The figure confirms its good stability of M_s (approximately 0.2°C). Also, it can be seen in Figure 4.23(b) that there is a strong linear relationship

² Equivalent to the magnitude of constrained stress applied during thermal cycling.

³ These stress levels fall under below, above, and farther above the first yield stress, σ_y , as shown in Figure 4.1, which roughly covers the distinctive feature of martensite deformation in equiatomic NiTi alloy.

4.4 Development of Internal Stress

Figure 4.23 (a) DSC curves showing the stability of M_s -temperature during twenty consecutive stress-free cycling. (b) Evolution of the M_s in relation to the magnitude of constrained stress and number of training cycles. (c) Cyclic effect on the characteristic gradient, $\Delta\sigma_{EXT}/\Delta M_s$.

established between M_s and external stress. Based on these observations, equation (4.2) is validated. From Figure 4.23(c), the characteristic gradient $\Delta\sigma_{EXT}/\Delta M_s$ as a function of number of training cycles N extrapolated shows a steady decline. A similar result was observed in Ti-Ni-Cu alloy [53].

Figure 4.24 shows the evolution of accumulated internal stress estimated by the equation 4.2. It is to note that, in view of SATWME, any change in M_s between 0th (i.e. prior to thermal cycling) and 1st training cycle is driven by the external stress, not by the internal stress [53]. More specifically, aside from the fact that internal stress develops due to reorientation of martensite variants via pre-straining [86], the

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Figure 4.24 Estimation of internal stress developed during the five training cycles under conditions of 50, 200, and 400 MPa constrained stress.

Figure 4.25 Stress-assisted two-way memory strain as a function of martensitic strain generated during training cycles under various constrained stress conditions; the dashed line indicates that the maximum ϵ_{SATW} is achieved at about 13% ϵ_{MA} .

4.4 Development of Internal Stress

development of internal stress due to cyclic accumulation of ε_{IR} takes place from 2nd training cycle onwards. The result presented in Figure 4.24 reveals that under low external stress of 50MPa, the internal stress was merely increased to 8.6MPa and it showed sign of saturation at 5th cycle. Applying 200MPa, on the other hand, was particularly favorable in developing internal stress in that it increased significantly to 47.7MPa. Its increment being paramount especially at the 2nd cycle could rationalize the generation of maximum ε_{SATW} in the preceding cycle (Figure 4.3). On the contrary, applying 400MPa resulted in a slow but steady increase in internal stress reaching about 50MPa at 5th cycle. This steady increase partially explains the corresponding increase of ε_{SATW} , as observed in Figure 4.15.

In order to further investigate on the mechanism of attaining maximum SATWME, the graph of Figure 4.15 has been reconstructed with respect to the ε_{SATW} as a function of ε_{MA} and number of training cycles, N , as shown in Figure 4.25. It can be seen that the strain curve tends to shift upwardly to the right, enlarges its parabolic shape and stabilizes gradually as the number of cycle increases. It is also noticed that the maximum ε_{SATW} was generated at about 13% ε_{MA} (indicated by the dashed line in the figure), which coincides extremely well with the result obtained under direct application of 13% pre-strain and 200MPa constrained stress (Figure 4.9). Based on this observation, it is reasonable to equate the progress of ε_{MA} with the magnitude of pre-strain. That is, these two deformation parameters can be categorized into a single parameter: *total strain deformation* as proposed earlier.

The experimental observation further implies that from the viewpoint of achieving maximum SATWME, it is independent of deformation procedures, whether is it initiated by the fixed pre-strain with variable constrained stress condition or by

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Figure 4.26 Effect of martensitic strain generated under 50, 200, and 400MPa constrained stress on the development of internal stress; the dashed line indicates that at 13% ϵ_{MA} the optimum internal stress can only be generated under 200MPa constrained stress.

the fixed constrained stress with variable pre-strain condition.

As we saw the emergence of maximum SATWME at 13% deformation, the importance for applying optimum constrained stress in achieving maximum ϵ_{SATW} can be well explained by the development of internal stress. Figure 4.26 shows the graph reconstructed with respect to internal stress as a function of ϵ_{MA} and constrained stress. It becomes clear that at 13% ϵ_{MA} , which is denoted by the vertical dashed line in the figure, a maximum value of internal stress can only be established at 200MPa; internal stress measured approximately 45MPa, which is significantly larger than that of 3.6MPa generated under 400MPa. For the case of 50MPa, obviously it is not a probable scenario to reach 13% ϵ_{MA} . Thus, based on these experimental evidences, it can be rationalized that attaining maximum SATWME under 200MPa occurs as a

4.4 Development of Internal Stress

consequence of the progress in total strain deformation toward optimum (i.e. cyclic shift of ε_{MA} in this case), under which produces the optimum internal stress.

After having firmly stated the deformation procedure independence of achieving maximum SATWME, it would be of particular importance to know whether the direct application of 13% pre-strain and single 200MPa constrained cycling produces the same amount of internal stress as the one produced by the cyclic shift of ε_{MA} . Previous study [222] showed that the value of internal stress was estimated to be 15MPa in the former training condition, which is significantly smaller than that of accumulated internal stress via latter condition. The estimation, however, requires reassessment since the values of internal stress were calculated with respect to the magnitude of pre-strain, not to the *total strain deformation*.

As highlighted in Section 4.2.2, although equal degree of pre-strain was applied to 50, 200, and 400MPa constrained stress conditions, the strain deformation progresses further upon constrained thermal cycling. For this reason, inaccuracy may be caused upon the M_s -external stress relation that they are not linearly related when plotted against the pre-strain values (cf. Figure 7 of previous study [222]). Figure 4.27 shows the revised estimation of internal stress, which is given as a function of total strain deformation (details of the revised estimation are shown in Appendix E). It can be seen that direct application of 13% deformation produces slightly less than 20MPa internal stress. This value is still considerably smaller than that of accumulated internal stress developed via successive training cycles (45MP). Experimental evidence herein underlines the fact that the generation of maximum SATWME is not attributed to the development of maximum internal stress.

It is also noticed from Figure 4.27 that the 200MPa curve virtually intersects with 50MPa curve at 13% deformation, followed by an abrupt increase of internal stress

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Figure 4.27 Revised estimation of internal stress for the fixed constrained stress condition (Test (2a)).

with further deformation to 18%. This sudden increase in internal stress was clearly reflected by the increase of ε_{IR} (Figure 4.11), which indicates that introduction of dislocations beyond 13% deformation became no longer effective in improving SATWME.

By comparing the 50MPa curve shown in Figure 4.27 with that in Figure 4.24, it becomes clear that pre-straining⁴ increases the amount of internal stress more effectively than the repeated cyclic deformation. In the case of pre-straining, the value of internal stress increased to a maximum of 18.5MPa at 13% deformation, where the largest ε_{SATW} was generated (Figure 4.10). Further deformation to 18%, however, resulted in the sharp decline of internal stress reaching 2.5MPa, and so did the decline of ε_{SATW} . Incidentally, the trend displayed in the ε_{SATW} under 50MPa coincides extremely well with that of TWME. A previous study [28] demonstrated that the

⁴ Note that majority of the degree of total strain deformation progressed under 50MPa cycling is caused by the pre-straining (see Table 4.1).

4.4 Development of Internal Stress

maximum TWME was achieved at about 13% pre-strain and further deformation caused decline in the two-way memory strain. In this respect, it is concluded that the mechanism that leads to the development of maximum TWME is driven by the optimum magnitude of internal stress. Furthermore, in terms of generating maximum TWME and SATWME, having witnessed their strong agreement not only in the deformation (i.e. 13%) but also in the internal stress implies that the development mechanisms of TWME are related very closely with SATWME at their maximum level.

For the case of 400MPa, it becomes apparent from Figure 4.28(b), which is reconstructed from Figure 4.25 with respect to 400MPa, that ε_{SATW} generated at 18% ε_{MA} is about 2.6%. In contrast, ε_{SATW} due to direct application of 18% deformation is about 3.3%, as shown in Figure 4.28(a). Thus, under higher constrained stress condition such as 400MPa, direct deformation is more effective in promoting SATWME. The discrepancy of ε_{SATW} in these two conditions is partly attributed to internal stress; direct 18% deformation generates internal stress of 27.2MPa (Figure 4.27), whereas ε_{MA} driven 18% deformation generates 12.5MPa (Figure 4.26).

Figure 4.28 Characteristic of stress-assisted two-way memory strain under 400MPa, the graphs reconstructed from: (a) Figure 4.10; and (b) Figure 4.25.

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4.5 Further Remarks and Summary

The experimental results concerning the full transformation and two-way shape recovery characteristics were presented in this chapter. Some aspects of stress, strain, and thermal cycling factors affecting the development mechanisms of SATWME were investigated.

One of the most significant factors that influence the magnitude of stress-assisted two-way memory strain, ε_{SATW} , is the magnitude of constrained stress. As discovered in Section 4.1.1, the value of ε_{SATW} increases to its maximum at 200MPa and further increase in stress resulted in the sharp decline. Although the degree of pre-strain was fixed at 8%, the martensitic strain, ε_{MA} , measured at the completion of forward transformation indicated further propagation of deformation. The value of ε_{MA} varied greatly according to the degree of constrained stress applied, and the clear transition point appeared at 200MPa.

The fixed constrained stress experiments verified that the shape recovery characteristic of SATWME is influenced by the magnitude of pre-strain or ε_{MA} , whichever is dominant. The results show that the value of pre-strain was greater than that of ε_{MA} under low constrained stress, thus pre-strain was dominant in determining the SATWME. This scenario became the opposite with increasing constrained stress to 400MPa.

The importance for applying 200MPa constrained stress in achieving maximum SATWME was rationalized by the development of internal stress. Based on the graph plotted with respect to internal stress as a function of ε_{MA} and constrained stress, it was clear that at 13% ε_{MA} , maximum internal stress can only be established under 200MPa constrained cycling. Nevertheless, internal stress developed via single

4.5 Further Remarks and Summary

200MPa cycling with direct application of 13% pre-strain was significantly smaller than that of accumulated internal stress developed via ε_{MA} . Hence, it is concluded that the generation of maximum SATWME is not attributed to the development of maximum internal stress.

For the cases of 50 and 400MPa constrained stress, pre-straining increased the amount of internal stress more effectively than the repeated cyclic deformation. The change in the magnitudes of internal stress was partially responsible for the corresponding increase/decrease of ε_{SATW} . For the case of 400MPa in particular, the greater the amount of internal stress developed, the larger is the recovery of SATWME.

The trend displayed in ε_{SATW} under 50MPa constrained stress agrees well with that of TWME. Having witnessed further agreement not only in the value of martensite deformation (i.e. 13%) but also in the value of internal stress in generating maximum SATWME, it is concluded that the development mechanisms of TWME and SATWME are strongly correlated at their maximum level.

The thermomechanical correlations of TWME and SATWME will be further explored in Chapters 5 and 6.

CHAPTER 5

Partial Transformation and the Shape Recovery Characteristics

The influence of partial transformation on the two-way shape recovery characteristics will be examined in this chapter. Similar to those three thermomechanical test conditions investigated earlier for the full transformation (Test (1a), (2a) and (3a)), the effect of partial transformation will be analyzed systematically by adjusting the amount of retained martensite (%RM) in the reverse transformation under constraint. Considering the expected emergence of two-step reverse transformation due to partial transformation, the accommodation mechanisms of distinctively oriented martensite variants that are accountable for further plastic deformation (i.e. reflected by the irrecoverable strain) and order of reverse transformation will be discussed.

In Section 5.1, fixed pre-strain with 50, 200 and 350MPa constrained stress conditions (Test (1b)) will be considered. The experiments were designed in such a way as to cover the broad range of martensite deformation regions II-IV (*see* Chapter 1, Section 1.2.2). The correlation between SATWME and TWME will be analyzed with respect to martensitic strain.

The correlation between SATWME and TWME will be analyzed further from the perspective of generating maximum memory effect under full and partial

CHAPTER 5. Partial Transformation and the Shape Recovery Characteristics

transformation conditions (Test 2(b)) in Section 5.2. In view of previous studies conducted for examining the influence of martensite pre-deformation on the transformation strain and the TWME [28, 49], thermomechanical relationship between SATWME and the TWME will be discussed. A key point of discussion will include an experimental approach to firmly establish the factors affecting the SATWME and TWME. In general, it is known that these memory effects are affected by the martensite pre-deformation, constrained stress and number of repeated thermal cycling.

Results obtained in Sections 5.1 and 5.2 will form the basis of identifying microstructural and macromechanical mechanism responsible for the TWME, i.e. martensitic strain and the TWME will be presented in Section 5.3, and relation between the type of internal stress formed and the two-way memory behavior will be presented in Section 5.4.

In Section 5.5, the effect of partial transformation on the SATWME and TWME will be examined further by increasing the number of training cycles (Test (3b)). Particular attention will be paid on the appearance and disappearance of two-step reverse transformation. Meanwhile, the rearrangement of dislocations and martensite variant re-configuration due to full/partial transformation are discussed in light of M_s -temperature change, presented in Section 5.6.

The established factors will then be applied to a post-trained thermodynamic analysis in effort to further examine thermomechanical correlation between SATWME and TWME in Chapter 6.

5.1 Test (1b): Effect of Partial Transformation on the SATWME and TWME in Fixed Pre-strain Condition

5.1.1 Stress-Strain Analysis

Figure 5.1 shows the stress-strain curves of the as-annealed specimen (diameter = 0.185mm) isothermally deformed at room temperature under tension to 4% pre-strain, as indicated by the dashed line in the figure. After completion of unloading to zero stress, the specimens were reloaded to 50, 200 and 350MPa stress level.

Similar to what was observed earlier for the wire diameter = 0.508mm (*see* Chapter 4, Section 4.1.1), the stress-strain curves showed a first yield at about 140MPa, followed by the emergence of stress-plateau with length stretching approximately 5.5%. Abrupt rise of stress with the increase of deformation was evident immediately after the stress-plateau. Reloading to 200 or 350MPa causes the specimen to enter into a further detwinning region (causing about 8 or 10% strain pre-deformation), whereas reloading to 50MPa remains inside the plateau region.

Figure 5.1 Stress-strain curve obtained at room temperature for as-annealed NiTi wire (diameter = 0.185mm).

5.1 Test (1b): Effect of Partial Transformation on the SATWME and TWME

5.1.2 Strain-Temperature Analysis (50MPa)

The partial reverse transformation of pre-strained specimen involves the retention of detwinned/reoriented martensite variants. To characterize the influence of retained martensite on the SATWME and TWME, various fractions of retained martensite (%RM) were imposed through arresting at temperatures between A_s and A_f during 1st heating (cf. Figure 3.8(a)). In the case of 50MPa constrained cycling condition, the amount of %RM varied between 0 and 69%RM. In effect, 0%RM indicates the fully reverse transformed condition.

Figure 5.2 shows the development of SATWME and TWME subjected to 50MPa constrained stress with various fractions of retained martensite. Two observations are noteworthy in Figure 5.2(a). Firstly, two-step reverse transformation appeared in the 1st heating for all cases. The first-step is related to the reverse transformation of the self-accommodating martensite, since their transformation temperatures (A_s^{SA}, A_f^{SA}) matches closely to the as-annealed (*see* Figure A.3). The second-step occurring at higher temperature (A_s^{DT}, A_f^{DT}) thus pertains to the reverse transformation of the detwinned martensite. Such two-step reverse transformation arises from the localized deformation of martensite, i.e. with 4% pre-strain and under 50MPa constrained stress the deformation magnitude is within the stress-plateau region (Figure 5.1), in which deformations are localized [31, 218]. Such localized martensite deformation induces two-step reverse transformation [235]. Secondly, following the two-step reverse transformation is the emergence of two-step forward transformation occurring especially under low %RM. It seems that the first-step is followed immediately by the second-step of forward transformation (i.e. $M_s' \rightarrow M_s$).

Once the specimens are subjected to partial transformation (1-69%RM) in the 1st heating, a clear two-step recovery occurred in the 2nd heating (Figure 5.2(b)). It can be

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Figure 5.2 Strain-temperature curves subjected to 4% pre-strain, 50MPa constraint stress and with various fractions of retained martensite: (a) curves recorded during 1st heating and cooling under constraint, labeling of various transformation temperatures: A_s^{SA} , A_f^{SA} , and A_s^{DT} , A_f^{DT} , austenite start, finish temperatures of the self-accommodated martensite and detwinned martensite, respectively; M_s' and M_s , martensite start temperature in the first-step and second-step of forward transformation; (b) curves recorded during constrained 2nd heating, unloading and stress-free cooling and heating.

5.1 Test (1b): Effect of Partial Transformation on the SATWME and TWME

Figure 5.2 Continued from the last figures: (c) effect of martensitic strain on the magnitudes of stress-assisted two-way memory strain and two-way memory strain.

seen that both the magnitudes of SATWME (ϵ_{SATW}) and TWME (ϵ_{TW}) decreases with increasing volume fraction of retained martensite. The decrease of ϵ_{SATW} and ϵ_{TW} are further analyzed with respect to the magnitude of martensitic strain, ϵ_{MA} , as shown in Figure 5.2(c). It becomes apparent that slight changes in the ϵ_{MA} due to retained martensite directly affected on the ϵ_{SATW} and ϵ_{TW} ; the result indicated the correlation of their magnitudes to martensite deformation.

Under constrained cooling, the martensitic strain decreases slightly with increasing retained martensite, i.e. the more the microstructure participating austenite $\rightarrow$ stress-assisted martensitic transformation, the more the formation of preferentially oriented martensite variants, thus the larger the ϵ_{MA} . This preferential formation is responsible for the small increase in SATWME and TWME from the case of partial transformation to full transformation.

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5.1.3 Strain-Temperature Analysis (200MPa)

Figure 5.3 shows the development of SATWME and TWME subjected to about 8% strain pre-deformation, 200MPa constraint stress and with various fractions of retained martensite. Unlike the previous case of 4% pre-strain and 50MPa constraint stress, the strain-temperature reveals no sign of two-step transformation in the 1st heating and cooling (Figure 5.3(a)). However, the magnitude of martensitic strain, ε_{MA} , decreases significantly due to an increase of %RM. Following the decrease of ε_{MA} is the decrease of both ε_{SATW} and ε_{TW} magnitudes (Figure 5.3(b)). With 13%RM condition, for example, the magnitude of both ε_{SATW} and ε_{TW} decreases by about 0.5%. For the SATWME, the two-step reverse transformation during 2nd heating is characterized by the relatively large recovery in the first-step occurring between A_s' and A_f' temperatures, as compared to the smaller recovery in the second-step between A_s and A_f . This observation indicates that the latter recovery is attributed to the reverse transformation of retained martensite. Similar to the case of 4% pre-

5.1 Test (1b): Effect of Partial Transformation on the SATWME and TWME

Figure 5.3 Strain-temperature curves subjected to about 8% pre-deformation, 200MPa constraint stress and with various fractions of retained martensite: (a) curves generated during 1st heating and cooling under constraint; (b) curves generated during constrained 2nd heating, unloading and stress-free cycle; labeling of various transformation temperatures: A_s' , A_f' and A_s , A_f , austenite start, finish temperatures in the first-step and second-step of reverse transformation, respectively; and (c) effect of martensitic strain on the magnitudes of stress-assisted two-way memory strain and two-way memory strain.

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strain and 50MPa constraint stress, changes in the ε_{MA} due to retained martensite directly affected on the ε_{SATW} and ε_{TW} , as shown in Figure 5.3(c). Thus, direct correlation between SATWME and TWME to martensite deformation is again established.

Compared with the previous study [62], it is noticed that the effect of partial transformation on SATWME and TWME varies depending on a magnitude of pre-strain applied. As it turned out later, the degree of reduction in ε_{SATW} would be minimized if low pre-strain is applied, whereas the opposite trend is true for the ε_{TW} . These two-way memory behaviors will be further investigated by considering other pre-strain conditions in Section 5.2.

5.1.4 Strain-Temperature Analysis (350MPa)

Figure 5.4 shows the development of SATWME and TWME subjected to about 10% strain pre-deformation, 350MPa constraint stress and with various fractions of retained martensite. The inset in Figure 5.4(a) shows the details of retaining martensite process during 1st heating. For an ease of comparison and clarity, all the strain-temperature curves shown in Figure 5.4(b) have been normalized to zero strain at the completion of unloading. Evidently, all the magnitudes of ε_{MA} , ε_{SATW} and ε_{TW} decrease with increasing %RM. It is also evident that the direct correlations of ε_{SATW} and ε_{TW} as a function of ε_{MA} are established, as shown in Figure 5.4(c). Furthermore, it is noticed that detecting clear two-step reverse transformation become difficult with increasing constrained stress. That is, although for those cases subjected to 50MPa with 16%RM (Figure 5.2(b)) and 200MPa with 13%RM (Figure 5.3(b)) showed two-step reverse transformation, the two-step is barely seen under

5.1 Test (1b): Effect of Partial Transformation on the SATWME and TWME

Figure 5.4 Strain-temperature curves subjected to about 10% pre-deformation, 350MPa constraint stress and with various fractions of retained martensite: (a) curves generated during 1st heating and cooling under constraint; (b) curves generated during 2nd heating, unloading and stress-free cycle.

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Figure 5.4 Continued from the last figures: (c) effect of martensitic strain on the magnitudes of stress-assisted two-way memory strain and two-way memory strain.

350MPa with 11%RM (Figure 5.4(b)).

Distinct from the results of 50 and 200MPa, the result obtained under 350MPa show peculiar feature of the strain-temperature curve, as shown in the inset of Figure 5.4(b). A shape change opposite to the loading direction is clearly discernible during the course of TWME and its magnitude increases with increasing %RM. This result can be explained with reference to Figure 5.5. The original undeformed specimen has gauge length 55mm (Figure 5.5(a)). Given that the specimen was loaded in tension (Figure 5.5(b)), the reverse martensite (M) $\rightarrow$ austenite (A) transformation causes contraction (Figure 5.5(c)), whereas the forward $A \rightarrow M$ transformation causes expansion (Figure 5.5(d)). Thus, it would be least expected to observe a contraction during cooling. However, a previous study [57] demonstrated that as the constrained stress intensifies, it increases the likelihood of forming an intermediate R -phase

5.1 Test (1b): Effect of Partial Transformation on the SATWME and TWME

Figure 5.5 Schematics of deformation and shape recovery orientation of as-annealed NiTi specimen (without R -phase transformation).

(rhombohedral phase). In the present case, the formation of R -phase has been cross-examined by DSC, as shown in Figure 5.6. Two peaks were detected during cooling irrespective of %RM conditions. Also, these peaks remain in the same position even after multiple cycles, as shown in Figure 5.7. More importantly, it is evident that the R -phase peak, R_p , appeared near 45°C corresponds well with the occurrence of contraction (inset of Figure 5.4(b)). Thus, based on these observations, it is ascertained that the contractive recovery in the course of TWME is attributed to the formation of R -phase.

It has been suggested that the interaction between R -phase and martensite interfaces bring about an opposing internal back stress, which intensifies with increasing fraction of retained martensite [192]. As has been demonstrated in Section 4.4, the development of internal stress as a function of %RM can be analyzed based on the change of M_s -temperatures as shown in Figure 5.8. It has been reported [22]

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Figure 5.6 DSC measurement of about 10% pre-deformed specimens undergone 350MPa constrained thermal cycling with different fractions of retained martensite: (a) 6%RM; and (b) 94%RM; labeling of various transformation peaks: A_p , austenite peak in the reverse transformation; R_p and M_p , R -phase and martensite peak in the forward transformation.

Figure 5.7 DSC exothermic measurement of cyclic behavior of about 10% pre-deformed specimens undergone 350MPa constrained thermal cycling with different fractions of retained martensite: (a) 6%RM; and (b) 94%RM.

that certain dislocations network impede the interface movements in the martensite and R -phase by forming back stress around them, resulting in a decrease of M_s . Evidently, for the case of 350MPa, there is a continuous decrease of M_s with increasing %RM, implying the increase of internal back stress. Also, the observation that the transformation enthalpy, ΔH , decreases from the as-annealed (Figures A.3 and 5.6) and that the further decrease of ΔH occurs due to increased %RM is consistent with the observation of increased internal stress effect on the transformation heat [236].

5.1 Test (1b): Effect of Partial Transformation on the SATWME and TWME

Figure 5.8 Effect of retained martensite on the M_s -temperature measured at 1st cooling for the 4% pre-strain and various constraint stress conditions.

5.2 Test (2b): Effect of Partial Transformation on the SATWME and TWME in Fixed Constrained Stress Condition

As highlighted in Section 5.1.3, there exists a sensitivity of partial transformation on the magnitudes of SATWME and TWME. This sensitivity is dependent on a degree of martensite deformation. In this section, the following two aspects of SATWME and TWME are presented: firstly, presenting results of the effect of martensite deformation (8-23% pre-strains) on the SATWME and TWME under 200MPa fully transformed condition, and secondly, presenting results of the effect of partial transformation on the characteristic of SATWME and TWME, and correlation of their magnitudes to martensite deformation. On the basis of these results, a microstructural mechanism responsible for the TWME is further clarified and a relation between the type of internal stress formed and the two-way memory behavior is discussed.

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5.2.1 Stress-Strain Analysis

Figure 5.9 shows the stress-strain curves of the as-annealed specimen deformed in tension to 8-23% pre-strains at room temperature, followed by unloading and reloading to 200MPa. The stress-strain curves can be divided into four regions (see Chapter 1, Section 1.2.2). The elastic region (marked by I) mainly consists of self-accommodated martensite twins. After deformation to about 1.5% strain, it surpasses the region I and proceeds to the partial detwinning region (marked by II). Some defects are generated in region II to accommodate the detwinning and martensite reorientation processes [31, 221]. Deformation to 8% strain enters into the further detwinning region (marked by III). Strain deformation to 13% is likely to reach the end of region III. Straining even further to 18 and 23% enters into massive dislocation region (marked by IV). The formation of dislocations has been well acknowledged to affect the TWME [80, 87, 170].

Figure 5.9 Stress-strain curve of as-annealed NiTi wire (diameter 0.185mm) subjected to various pre-strain magnitudes and reloading to 200MPa.

5.2 Test (2b): Effect of Partial Transformation on the SATWME and TWME

5.2.2 Effect of Martensitic Strain on SATWME and TWME

Subsequent to the martensite pre-deformation, the constrained thermal cycling was performed to characterize the SATWME and TWME. Figure 5.10 shows the strain-temperature curves of 8-23% pre-strained specimen under 200MPa constrained stress. It can be seen that the martensitic strain, ε_{MA} , measured at the end of 1st cooling tends to surpass the initial pre-strain level. In the preceding sections, it has been observed that the magnitude of ε_{MA} is a key factor determining the magnitudes of SATWME and TWME. Figure 5.11 summarizes the influence of ε_{MA} on the magnitudes of SATWME and TWME. Similar to what was observed earlier in Figure 5.3(c), SATWME and TWME showed a strong correlation of their magnitudes as a function of martensitic strain. This observation is also in agreement with previous study [60,

Figure 5.10 Strain-temperature curve of full transformation cycles subjected to various pre-strain magnitudes and 200MPa constraint stress: (a) 8% pre-strain; (b) 13% pre-strain; (c) 18% pre-strain; and (d) 23% pre-strain.

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Figure 5.11 Effect of martensitic strain on the development of SATWME and TWME.

61]. After reaching maximum value near 20% ϵ_{MA} , further martensite deformation caused decrease of both ϵ_{SATW} and ϵ_{TW} .

In addition to correlation between SATWME and TWME, it is worth comparing the result (Figure 5.11) with those observed earlier for the thicker wire results (Figures 4.9 and 4.10). Considering 13% pre-strain for both cases, ϵ_{SATW} is found to be larger for the thinner wire (about 5.0%) than that of thicker wire (4.3%). The difference in values is likely related to the stronger texture formed in the thinner wire [237]. Furthermore, in comparison with previous study [28], it is noticed that there is discrepancy in the pre-strain for achieving the maximum TWME. Such discrepancy is ascribed to the response of stress-strain curves: with reference to Figures 2(a) and 8 of the previous study [28], maximum TWME is achieved at about 13% pre-strain, at which deformation enters into massive dislocation region. From Figure 5.9 of the

5.2 Test (2b): Effect of Partial Transformation on the SATWME and TWME

present study, it is apparent that the equivalent deformation is achieved at about 18% pre-strain, thus, explains the discrepancy in the pre-strain magnitude for generating maximum TWME.

5.2.3 Strain-Temperature Analysis (8-23% pre-strains)

To gain further insight into the two-way memory behaviors due to partial reverse transformation, a series of strain-temperature curves highlighting the development of SATWME and TWME (between 8-23% pre-strains and under 200MPa constraint stress) with various fractions of retained martensite are obtained and shown in Figure 5.12. It can be seen that the decrease of ϵ_{SATW} due to partial reverse transformation gets more pronounced with increasing pre-strain, as highlighted on near 15%RM

Figure 5.12 A series of strain-temperature curves subjected to 200MPa constraint stress and with various fractions of retained martensite and magnitudes of pre-strain: (a) 8%; (b) 13%; (c) 18%; and (d) 23%.

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conditions. More specifically, the value of ε_{SATW} decreases by about 0.5% for the 8% pre-strain, 1.0% for the 13% pre-strain, and 1.8% for both the 18 and 23% pre-strains (from Figures 5.12(a) to (d)). Contrasted to the pronounced decrease of SATWME, TWME is essentially alleviated with increasing pre-strain. In the two-step reverse transformation, the transformation temperature interval for the first-step (heating from A_s' to A_f , measured typically 30°C) is observed to remain almost unchanged, being independent of the pre-strain conditions. On the contrary, the temperature interval in the second-step (heating from A_s to A_f) seems to diminish with increasing pre-strain.

Figure 5.13 summarizes the effect of partial reverse transformation on the magnitude of martensitic strain, ε_{MA} , achieved during constrained cooling with various pre-strain conditions that helps to understand the changes in ε_{SATW} . Evidently, under 8% pre-strain, all the ε_{MA} values are within deformation region III (except for

Figure 5.13 Effect of retained martensite on the magnitude of martensitic strain for the specimens subjected to various pre-strain magnitudes and 200MPa constraint stress.

5.2 Test (2b): Effect of Partial Transformation on the SATWME and TWME

the 0%RM), whereas for the 13% pre-strained specimen ε_{MA} enters into region IV at low %RM. Clearly, the acute decrease of ε_{MA} is notable until about 15%RM for all cases and the gradual decrease follows thereafter with further increase in %RM. Focusing on the results near 15%RM, it seems that the pronounced decrease of ε_{SATW} (Figure 5.12) due to partial reverse transformation is ascribed to the corresponding acute decrease of ε_{MA} .

It is generally accepted that the deformation beyond stress-plateau (region III and IV) results in the further detwinning of martensite and increased dislocation density [29-31, 218, 221]. It has been observed in DSC investigations that larger the martensite deformation the farther the distinct separation of two transformation peaks [238]. In the present study, it has been demonstrated that undergoing partial transformation evokes two-step reverse transformation. From Figure 5.12, it is noted that these evoked steps become wider apart (between A_s and A_f' temperatures as indicated by the open-arrow) as the pre-strain increases. Previous results [62] have suggested that the separation of A_s - A_f' is caused by the orientation mismatch of the two different types of martensite variants distinctively oriented. Thus, in addition to the changes in ε_{MA} , the larger decrease of SATWME results from a pronounced difficulty in accommodating differently oriented martensite variants. Such orientation differences are required to accommodate plastically for maintaining the integrity of the matrix [28].

5.2.4 Summary

Figure 5.14 and 5.15 respectively summarizes the effect of retained martensite on SATWME (ε_{SATW}) and TWME (ε_{TW}) under 200MPa constrained stress and with

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Figure 5.14 Effect of retained martensite on the magnitude of stress-assisted two-way memory strain for the specimens subjected to various pre-strain magnitudes and 200MPa constraint stress.

Figure 5.15 Effect of retained martensite on the magnitude of two-way memory strain for the specimens subjected to various pre-strain magnitudes and 200MPa constraint stress.

5.2 Test (2b): Effect of Partial Transformation on the SATWME and TWME

various pre-strains. 4% pre-strain result is also embedded in the figures for comparison. It can be seen that the value of ε_{SATW} decreases almost linearly with increasing %RM for 4 and 8% pre-strained samples. The decreasing trend of 4% pre-strain is almost identical to 8% pre-strain, since its pre-deformation reaches near 8% upon reloading to 200MPa (Figure 5.1). When the pre-strain increased to 13%, ε_{SATW} turned into a nonlinear decrease. Further increase in the pre-strain to 18 and 23% caused much significant nonlinear decrease of ε_{SATW} reaching 2.42% at 73%RM and 1.61% at 71%RM, respectively, as indicated in the figure. For the TWME, we note from Figure 5.15 that the 4 and 8% pre-strained specimens showed continuous decrease of ε_{TW} with increasing %RM, which seems to correspond well to the decrease of ε_{SATW} in Figure 5.14. However, the trend of ε_{TW} as a function of volume fraction of retained martensite is changed by increasing pre-strain to 13, 18 and 23%. It shows a gradual rise with further increase in %RM, despite an abrupt change at near 15%RM. Important to highlight is that the ε_{TW} does not show direct causal relation with the ε_{SATW} .

Another important feature to highlight from the results (Figures 5.14 and 5.15) is that the magnitude of TWME can be larger than that of SATWME: with 23% pre-strain, the value of ε_{TW} is 1.78% and only 1.61% for ε_{SATW} (at 71%RM). In contrast, with 18% pre-strain, the value of ε_{SATW} tends to be larger than that of ε_{TW} and the same tendency persist for the 8 and 13% pre-strains. The result concerning the 23% pre-strain suggests that the microstructures not promoting the SATWME may not necessarily be detrimental to the development of TWME.

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5.3 Martensitic Strain and the TWME

The experimental results presented thus far demonstrate that, in the partial transformation condition, the recovery magnitude correlations of SATWME and TWME as a function of martensite deformation are not always established. Contrasted to the 50 and 350MPa results (Figures 5.2(c) and 5.4(c)), the decrease of ε_{MA} under 200MPa has led to complex variations of TWME, i.e., transition from continuous decrease to combination of decrease and increase in ε_{TW} occurred due to increasing pre-strain from 8% (Figure 5.15). The occurrence of such transition in TWME lies in the martensite deformation mechanism, explained with reference to Figure 5.13 as follows:

- With 8% pre-strain, regardless of %RM, constrained thermal cycling leads to the further increase in martensite deformation with all the ε_{MA} values exceeding the initial 8% pre-strain. Based on the fact that deformation is within region III and that the highest ε_{TW} is obtained when martensitic strain is in region IV, we would envisage that the optimum condition is yet to be reached; the decrease of ε_{TW} with increasing %RM is therefore directly related to the decrease of ε_{MA} .
- With 13, 18 and 23% pre-strains, in the range (0-15%RM), the ε_{MA} decreases to below respective pre-strain values with increasing %RM. Thus, the change in martensitic strain with further increasing retained martensite did not affect the ε_{TW} significantly. A plausible explanation to the abrupt drop of ε_{TW} (Figure 5.15) is that preferential growth of martensite variants favoring the TWME is disrupted by the plastic accommodation between stress-assisted and retained

5.3 Martensitic Strain and the TWME

martensite variants. This plastic accommodation process becomes the dominating factor to lower the magnitude of ε_{TW} .

- In the middle-range (15-54%RM), the amount of stress-assisted martensite (SAM) decreases with the increased fraction of retained martensite. Following the same thought that, constraint cooling favors the preferential growth of SAM to generate higher transformation strains [34], the decrease of SAM in this range is thus reflected by the decrease of ε_{MA} . Consequently, the plastic accommodation of stress-assisted and retained martensite variants would be alleviated, causing merely small changes to the ε_{TW} .
- With more than 54%RM, the effect of stress-assisted martensitic strain on the ε_{TW} is minimized because the value of ε_{MA} is now by far below the initial 13, 18 and 23% pre-strain. The mechanism that the improvement of ε_{TW} occurs in this higher retained martensite range is yet to be understood.

5.4 Microstructural Mechanism and the TWME

Macroscopically, the present results (Figures 5.2-5.4 and 5.12) point out that undergoing partial transformation results in a modification of strain-temperature curve. In this section, the essential qualitative features of the microstructural mechanism and the TWME are deduced by relating these modified macroscopic phenomena with dislocation structure and internal stress formation.

It has been shown [239] that undergoing partial transformation would act as a form of cold work by generating dislocations. In another study, Perkins and Bobowiec [240] have shown in microscopic observations that dislocation structures introduced by retained martensite are non-uniformly distributed. This means that the change of

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dislocation configurations due to retained martensite imposes heterogeneity in the local stress fields, a direct consequence of which leads to the formation of internal forward and back stresses.

Figure 5.16 shows a schematic model representing partial transformation process under 50MPa. On deforming the specimen within stress-plateau region causes a partial detwinning of self-accommodated martensite accompanied by some light defects forming at the grain boundary (Figure 5.16(a)). With the assumption that the reverse transformation occurs from left to right (undeformed martensite transforms first), constrained shape recovery upon heating proceeds from left to right. When arrested in the course of reverse transformation some fraction of detwinned martensite is retained (Figure 5.16(b)). In the subsequent cooling, forward transformation occurs in the opposite direction (Figure 5.16(c)). As preferential growth of martensite variants occurs with the rearrangement of dislocations, part of these dislocations will accumulate at mismatched boundary. The pile-up of dislocations at mismatched boundaries will then become the sources of internal back stresses, σ_i^B , which oppose the movement of dislocations in the forward transformation direction. However, with the help of internal forward stresses, σ_i^F , assisting the externally applied stress, martensitic strain ε_{MA} exceeds the start-strain upon completion of forward transformation.

Now, one may consider other partial transformation process, as illustrated in Figure 5.17. On deforming the specimen beyond stress-plateau region causes further detwinning of martensite and high density of dislocations (Figure 5.17(a)). Heating to the arrest-temperature causes some fraction of detwinned martensite to reverse transform into austenite (Figure 5.17(b)). In the subsequent cooling, the extent to

5.4 Microstructural Mechanism and the TWME

(a) Mechanical loading processes **(b) Constrained thermal cycling**

Figure 5.16 Schematic model showing the development of internal forward and back stresses for a specimen deformed within the stress-plateau region and thermal cycled under a constrained stress of 50MPa. (a) Mechanical loading processes: the specimen deformed in martensite to 4% strain unloaded and reloaded to 50MPa; microstructure comprised of self-accommodated and detwinned martensite, and a low density of dislocations at the grain boundaries. (b) Constrained thermal cycling: (i) shape recovery process under constrained heating, arrested before reaching the end of reverse transformation and (ii) nucleation and growth of stress-assisted martensite (SAM) in the presence of retained martensite under constrained cooling.

which ε_{MA} exceeds the start-strain will be higher for the 200 and 350MPa conditions, since the strain due to stress-assisted martensite (SAM) increases with increasing magnitude of constraint stress [24]. However, unlike the case of 200MPa where the

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(a) Mechanical loading processes

(b) Constrained thermal cycling

Figure 5.17 Schematic model showing the development of internal forward and back stresses for a specimen deformed beyond the stress-plateau region and thermal cycled under a constrained stress of 200MPa. (a) Mechanical loading processes: the specimen deformed to 10% strain, unloaded and reloaded to 200MPa; microstructure comprised of detwinned martensite and a high density of dislocations at the grain boundaries. (b) Constrained thermal cycling: (i) shape recovery process under constrained heating, arrested before reaching the end of reverse transformation and (ii) nucleation and growth of stress-assisted martensite (SAM) in the presence of retained martensite under constrained cooling.

dominance of σ_i^F prevails (Figure 5.17(c)), the increased dominance of σ_i^B under 350MPa impedes the interface movement of SAM and lowers the ε_{MA} substantially (Figure 5.4(a)).

5.4 Microstructural Mechanism and the TWME

As shown in Figure 5.18, retained martensite can cause variety of changes to the M_s -temperature for the various pre-strain and constrained stress conditions: 200MPa with 13, 18 and 23% pre-strain showed a prominent increase of M_s with increasing fraction of retained martensite. 350MPa, on the contrary, showed a continuous decrease of M_s (Figure 5.8). Based on earlier discussion (*see* Section 5.1.4), the increase and decrease of M_s can be associated with the formation of internal forward and back stress, respectively. It is suggested that, for a polycrystalline material, the predominance of internal forward stress over back stress or vice versa occurs due to asymmetry of slip [101, 241]. The present results clearly indicate that, in addition to highlighting the origin of TWME due to internal stress formations [85-87, 179], the high magnitude of TWME results from a dominant internal forward stress. The dominance of internal back stress, on the other hand, results in a decrease of TWME.

Figure 5.18 Effect of retained martensite on the M_s -temperature measured at 1st cooling for the 8-23% pre-strains and 200MPa constraint stress conditions.

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5.5 Test (3b): Effect of Partial Transformation on the SATWME and TWME in Repeated Cycles

Expanding on the thermomechanical analysis of the two-step reverse transformation, the effect of partial transformation on the SATWME and TWME in successive constrained cycles has been investigated. The detail of training conditions applied is as follows. The as-annealed NiTi specimens with diameter = 0.185mm were isothermally loaded in tension in fully martensitic state to 4% pre-strain, unloaded to zero stress and reloaded to 200MPa. While holding the stress constant at 200MPa, thermally-induced $M \leftrightarrow A$ phase transformations were repeated to complete 4 training cycles. Constrained load was released upon completion of 5th heating, followed by stress-free cycling to induce a TWME.

The influence of partial reverse transformation on SATWME and TWME was studied by considering four different cyclic conditions: i) full transformation; ii) partial transformation at 1st heating ($T_H = 140^\circ\text{C}$); iii) partial transformation at 1st and 3rd heating ($T_H = 140^\circ\text{C}$); and iv) partial transformation at 4th heating ($T_H = 125^\circ\text{C}$).

5.5.1 Strain-Temperature Analysis

The shape recovery behavior observed under various cyclic conditions is shown in Figure 5.19. To be noted is that the magnitude of irrecoverable strain denoted as ε_{IR} in Figure 5.19(a) excludes the portion of elastic strain recovery generated upon unloading, and therefore represents solely the generation of true plastic strain. Compared with the case of full transformation (Figure 5.19(a)), it is apparent that all the magnitudes of ε_{MA} , ε_{SATW} and ε_{TW} all decrease due to partial transformation, as summarized in Table 5.1. The amount of decrease in ε_{SATW} and ε_{TW} , however, is found to be substantially smaller than what was observed earlier in Test 1(b).

5.5 Test (3b): Effect of Partial Transformation on the SATWME and TWME

Figure 5.19 Strain-temperature curves generated due to various cyclic conditions: (a) full transformation; labeling of transformation temperature: M_s (1) – (4), martensite start temperature estimated at (N^{th}) cycle; (b) partial transformation at 1st heating.

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Figure 5.19 Continued from the last figures – curves generated due to various cyclic conditions: (c) partial transformation at 1st and 3rd heating, inset showing the details of M_s -temperature estimated at 3rd and 4th cycle; and (d) partial transformation at 4th heating.

5.5 Test (3b): Effect of Partial Transformation on the SATWME and TWME

Cyclic condition:	ε_{SATW} (%)	ε_{TW} (%)	$\Delta\varepsilon_{TW}$ (%)	ε_{MA} (%)	ε_{IR} (%)	$\Delta\varepsilon_{IR}$ (%)
i) Full transformation	5.95	2.14	-	21.35	1.34	-
ii) Partial trans. at 1 st heating	5.78	2.08	0.06	19.40	1.41	0.07
iii) Partial trans. at 1 st and 3 rd heating	5.61	1.91	0.23	17.67	1.54	0.20
iv) Partial trans. at 4 th heating	5.62	2.01	0.13	19.42	-	*0.13

*Estimated by the corresponding amount of reduction reflected in ε_{TW} .

Table 5.1 The magnitude of various strains recorded under four different cyclic conditions.

From Figures 5.14 and 15, the amount of decrease in ε_{SATW} and ε_{TW} due to partial transformation of 43%RM are about $[(4.87-3.77)/4.87] \times 100\% = 23\%$ and $[(1.55-0.84)/1.55] \times 100\% = 46\%$, respectively. Comparatively from Table 5.1, in the case of cyclic condition ii), the amount of decrease in ε_{SATW} and ε_{TW} are about $[(5.95-5.78)/5.95] \times 100\% = 2.9\%$ and $[(2.14-2.08)/2.14] \times 100\% = 2.8\%$, respectively. This apparent difference in shape recovery can be explained from the fact that the appearance of two-step transformation is a one-time only effect; its clear disappearance in the continued full transformation cycle suggests that the disrupted orientation of martensite variants were quickly repaired and rearranged into a preferential orientation guided by the constrained stress and aligned internal stress field.

Exploring further on the reduction of ε_{TW} due to partial transformation, the amount of $\Delta\varepsilon_{IR}$ and $\Delta\varepsilon_{TW}$ were quantified by their respective difference among the cyclic condition i) and the remaining conditions ii) – iv), as shown in Table 5.1. It is apparent that the value of $\Delta\varepsilon_{IR}$ corresponds extremely well with that of $\Delta\varepsilon_{TW}$, implying that any excessive plastic strain introduced by the partial transformation (i.e. reflected by $\Delta\varepsilon_{IR}$) directly removes the portion of recoverable strain in TWME.

CHAPTER 5. Partial Transformation and the Shape Recovery Characteristics

5.5.2 Correlation between SATWME and TWME

To highlight the correlation between SATWME and TWME, there is a clear trend that once the value of ε_{SATW} decreases so does the ε_{TW} . However, the trend does not necessarily show the comparative decrease in these memory effects, e.g. in the case of cyclic condition iii), the extent of decrease in ε_{SATW} and ε_{TW} due to partial transformation are about $[(5.95-5.61)/5.95] \times 100\% = 5.7\%$ and $[(2.14-1.91)/2.14] \times 100\% = 10.8\%$, respectively. Furthermore, comparing the cyclic conditions ii) and iv) in Table 5.1, although the values of ε_{MA} are found to be identical, the resultant values of ε_{SATW} and ε_{TW} are found to be non-identical in these cyclic conditions. Thus, as has been highlighted in the Test 2(b), the development mechanisms of SATWME and TWME are different when they are subjected to a certain partial reverse transformation condition.

5.6 M_s -temperature and Microstructural Mechanisms

Figure 5.20 summarizes the effect of retained martensite on the M_s -temperature evolved under various cyclic conditions. It can be seen that for the case of full transformation, M_s increases progressively with increasing number of training cycles. Compared with the case of full transformation, imposing partial transformation at 1st heating causes no conspicuous effect on the M_s , but it causes significant effect on the inclination of strain-temperature curve. The shallow inclination of the curve is associated not only with the increase in the microstructural anisotropy requiring prolonged undercooling to complete the transformation [242], but also with the stored elastic strain energy [24]. This stored energy is known to assist the reverse transformation [24, 95-97, 133, 199]. Indeed, the first-half of two-step transformation

5.6 M_s -temperature and Microstructural Mechanisms

Figure 5.20 The evolution of M_s -temperature as a function of number of training cycles undergone with various cyclic conditions.

gets promoted to take place at much lower temperature, whereas the start of remaining half of transformation is being prepositioned by the target temperature, T_H , (Figure 5.19(b)). Following the partial transformation imposed at 1st heating with full transformation in the next 2nd to 4th cycle resulted in the progressive increase of M_s .

In addition to partial transformation imposed at 1st heating, imposing another partial transformation at 3rd heating brings about noticeable rise and fall of M_s at 3rd and 4th cycle, respectively. Also, when partial transformation was imposed at 4th heating, M_s rises abruptly. To explain these phenomena, there is a possibility that the accommodation process of retransforming austenite $\rightarrow$ stress-assisted martensite (SAM) variant and the non-transformed SAM variant at later cycle momentarily disrupts the dislocation configurations that were established by the prior training cycles. The orientation mismatch among these SAM variants causes internal plastic deformation, which contributes to the rise of M_s . The decrease of M_s observed

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between 3rd and 4th cycle, however, arises from the dislocation rearrangement during which martensite variants reorient themselves into a preferential orientation. This microstructural rearrangement leads to the disappearance of two-step transformation, but the remnants of internal plastic deformation lower the SATWME and TWME.

5.7 Further Remarks and Summary

In this chapter, it has been demonstrated that the two-way shape recovery characteristics of as-annealed NiTi are largely influenced by the nature of thermal cycling. The results showed that imposing partial reverse transformation in the course of training process induces a two-step transformation in the next fully transformed strain-temperature curve.

In Test (1b), the correlation between SATWME and TWME determined for 50, 200 and 350MPa constraint stress is comparable to that observed in fully transformed condition: SATWME and TWME subjected to 8-23% pre-strains and under 200MPa constraint stress showed direct correlation of their recovery magnitude to a martensite deformation. The increase of martensitic strain through constrained cooling determined the increase of SATWME and TWME to their maximum achieved at near 20% strain. Further increase in martensitic strain caused decrease in these memory effects.

In Test (2b), the decrease of martensitic strain due to increase in fraction of retained martensite under 200MPa caused variation in TWME from continuous decrease to combination of decrease and increase in two-way memory strain. The variation occurs due to whether the martensitic strain exceeded the initial pre-strain magnitude to achieve the optimum martensite deformation for a TWME. When the

5.7 Further Remarks and Summary

martensitic strain decreases below the initial pre-strain magnitude with increasing retained martensite, it showed no significant effect on the TWME.

The underlying mechanism of TWME is associated with the internal forward and back stress formations. On the basis of M_s -temperature increase under 200MPa with increasing fraction of retained martensite, the high magnitude of TWME results from a dominant internal forward stress. On the contrary, a continuous decrease of M_s under 350MPa indicated the dominance of internal back stress. The formation of internal back stress hinders the progress of forward transformation to lower the martensitic strain, and thus the decrease of TWME.

In Test (3b), the appearance of two-step transformation is observed to be a one-time only phenomenon and it disappeared in the next full transformation. The disappearance of two-step transformation highlighted the occurrence of microstructural rearrangement driven by the internal stress field in the successive training cycles.

The role of internal forward and back stress formations on the mechanism of two-step transformation will be further explored in Chapter 7.

CHAPTER 6

Thermodynamic Analysis

To understand the development mechanism of SATWME and TWME further, the differential scanning calorimetry (DSC) measurement of post-trained specimens subjected to various test conditions (cf. Table 3.1) were carried out. DSC is capable of detecting the changes in thermal properties including transformation temperatures, interval and enthalpy and the possible formation of intermediate *R*-phase (X-ray diffraction technique will be employed to cross-examine the *R*-phase). As briefly highlighted earlier (*see* Chapter 4, Section 4.4), chemical component of the Gibbs free energy is invariably affected by the non-chemical components accompanying the transformation. Since the progression of thermoelastic behavior in shape memory materials is a condition of local balance between chemical and non-chemical energies, the energy balance condition may be expressed as [95]

$$\Delta G = \Delta H - T\Delta S + \Delta E_{el} + \Delta E_{fr} \quad (6.1)$$

where G is the total Gibbs free energy change, H and S are the changes in chemical component of enthalpy and entropy, respectively, T is the temperature, and the remaining two terms E_{el} , E_{fr} represent the changes in non-chemical component

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of elastic strain energy and irreversible frictional energy associated with the propagation of martensite-austenite phase transformation. Basing on thermodynamic theoretical foundation formulated in equation (6.1), the thermoelastic features of the post-trained specimens will be analyzed by paying close attention to the DSC measured transformation enthalpy, H . Note that all the DSC measurements were carried out by carefully following the procedures described earlier (*see* Chapter 3, Section 3.3).

This chapter will begin by evaluating quantitatively the changes in transformation temperatures and enthalpy detected under fully transformed conditions namely, Test (1a): Fixed pre-strain with variable constrained stress; Test (2a): Fixed constrained stress with variable pre-strain; and Test (3a): Fixed pre-strain and constrained stress with cyclic effects. Having observed the macromechanical correlation between SATWME and TWME, the thermodynamic correlation of these memory effects will be further discussed with respect to H and transformation temperature hysteresis.

In Section 6.2, the thermodynamic energy balance equations will then be applied to the measured H in effort to study the individual non-chemical components contributing to the lowering of chemical H . Of particular attention will be paid to the change in E_{el} and E_{fr} , which arises from the elastic accommodation of local transformation strain and internal stress fields present in the material. Careful analysis on the estimation of equilibrium temperature, where chemical and non-chemical components is balanced (i.e. $\Delta G_{ch} + \Delta G_{nch} = 0$), will be made in order to quantify the E_{el} and E_{fr} accurately under various treatment conditions. Transformation enthalpy formulations will then be discussed in Section 6.3, where it will be demonstrated that predominant mechanism leading to the decrease in H is the defects imparted through thermomechanical treatment.

CHAPTER 6. Thermodynamic Analysis

6.1 Analysis on Transformation Temperatures and Enthalpies

6.1.1 Test (1a): Fixed Pre-strain Condition

Figure 6.1 shows DSC thermogram of the post-trained NiTi specimens that have experienced single training cycle with 8% pre-strain and under 20, 100 and 300MPa constraint stresses. The endothermic curves in Figure 6.1(a) show that the martensite stabilization effect had occurred for the post-trained specimens, where their A_s -temperatures in the first heating increased from the as-annealed (67°C). In general, the martensite stabilization effect is frequently observed after ageing [243], cold-work [90, 202] and martensite pre-deformation [28, 33, 244, 245].

For the second heating, it clearly shows the tendency of the DSC curve shifting toward the left with the increase of constraint stress ($20 \rightarrow 100 \rightarrow 300\text{MPa}$), which indicates that the transformation temperatures are decreasing. Meanwhile, associated with the decrease of austenite peak temperature, A_p , the transformation enthalpy, H , decreases with increasing magnitude of constrained stress. The decrease of both transformation temperatures and enthalpy after subjected to constrained cycling was also reported in [51]. The temperature interval of reverse transformation, $A = A_s - A_f$,

Figure 6.1 DSC thermogram of the post-trained specimen subjected to one complete training cycle with 8% pre-strain and various constrained stress conditions: a) endothermic heat flow; and (b) exothermic heat flow.

6.1 Analysis on Transformation Temperatures and Enthalpies

on the other hand, amplifies from 11 to 15°C with increasing magnitude of constrained stress due to broadening of the peak. This suggests an increase of non-chemical energy barriers arising from the elastic strain energy and frictional resistance.

For the exothermic curves shown in Figure 6.1(b), only a little difference was observed between the first cooling and second cooling cycles. However, some distinctive features were seen in the result that multiple peaks emerged for the 300MPa specimen. The emergence of multiple peaks were suggested to be induced by the increase of internal plastic deformation [86] and the changes of dislocation configuration [238] that the initial single step transformation (austenite: $A \rightarrow$ martensite: M) would change into a two-step transformation ($A \rightarrow R\text{-phase} \rightarrow M$). To confirm the presence of R -phase, X-ray diffraction (XRD) analysis was performed for the 300MPa specimen at various temperatures cooling down from 120°C (austenite) to 20°C (martensite). The XRD pattern is shown in Figure 6.2. It can be seen that R -

Figure 6.2 XRD patterns obtained for the post-trained 300MPa specimen in the temperature range (20 - 120°C): R -phase peaks correspond to a space group $P3$ [247, 248] with indexes (202) and (022), $d = 2.03246$; or $P\bar{3}$ [247, 249, 250] with indexes (202) and (022), $d = 2.02951$ or 2.03317 .

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phase diffraction peaks are present at 45°C (near R_p of DSC result) and disappears upon further cooling to 20°C. The locations of R -phase diffraction peaks are in good agreement with previous study [246, 247].

Returning back to the DSC result (Figure 6.1(b)), by separating the location of the two peaks (M_p , R_p), it becomes apparent that the location of the M_p shift to a lower temperature with increasing magnitude of applied constrained stress. This indicates the lowering of forward transformation temperatures (M_s , M_f).

6.1.2 Test (2a): Fixed Constrained Stress Condition

Figure 6.3 shows the effect of various degrees of martensite deformation with fixed constrained stress of 50, 200 and 400MPa on the characteristic of DSC curves. Note that the total strain deformation mentioned here was determined by the magnitude of applied pre-strain or martensitic strain progressed during constrained cycling, whichever is higher (details *see* Appendix F). It is apparent from the endothermic curves shown in Figure 6.3(a), (c) and (e) that the first heating curve tend to shift to a higher temperature in comparison with the second heating curve. Moreover, some of the first heating curves showed serrated features and multiple-step transformation, which makes it difficult for an accurate interpretation of the results. Thus, we shall focus on the results produced in the second heating curve.

The reverse transformation temperatures remained practically unchanged especially for higher constrained stress conditions, while some changes were evident for the case of 50MPa (i.e. A_p tends to fluctuate with increasing deformation). Also, broadening of the reverse transformation peak occurs with increasing deformation, especially for the case of 50MPa.

6.1 Analysis on Transformation Temperatures and Enthalpies

Figure 6.3 The respective DSC endothermic and exothermic curves subjected to various degrees of total strain deformation and: a), b) 50MPa cycling; c), d) 200MPa cycling; and e), f) 400MPa cycling.

For the exothermic curves shown in Figure 6.3(b), (d) and (f), as expected, there was no apparent multiple-step transformation generated under 50MPa, while increasing magnitude of constrained stress to 200 and 400MPa resulted in a generation and distinct separation of the two-step transformation. It is of particular

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interest to note that the two-step appears to merge into single-step transformation when subjected to 13% deformation and 200MPa cycling. The sign of two-step transformation starts to reappear at 18.6% deformation (Figure 6.3(d)). The disappearance of two-step transformation is suggested to be caused by the rearrangement of dislocation configuration during the course of forward $A \rightarrow M$ transformation. In so doing alleviates the degree of inhomogeneity in the local stress field and the occurrence of internal plastic deformation [86]. This assertion is supported by the fact that the magnitude of internal stress decreases to a minimum of about 20MPa at 13% deformation under 200MPa cycling and increases with further deformation (cf. Figure 4.27). Thus, the reappearance of R -phase at 18.6% is connected to the increase of internal stress, which is likely to be caused by the introduction of additional dislocations [251].

6.1.3 Test (3a): Fixed Pre-strain and Constrained Stress with Increased Number of Cycles

The specimens subjected to four complete training cycles under 50, 200 and 400MPa show decrease of A_p (from 72 to 61°C), M_p (from 40 to 24°C) and H (from 17.2 to 11.1J/g) with increasing magnitude of applied constrained stress, as shown in Figure 6.4. Basing on the results of Figure 6.1(b) and 6.4(b), it appears that two peaks are detected at higher constrained stress (200, 300MPa). At even higher constrained stress (400MPa), the exothermic curve becomes flattened and shows wider separation of R -phase and M -phase.

The above observations are in good agreement with the case of cold-work [252]; R -phase peak emerged in a 2% thickness reduced specimen, and farther separation of R -phase and M -phase peaks occurred with increasing thickness reduction. Previous

6.1 Analysis on Transformation Temperatures and Enthalpies

Figure 6.4 DSC thermogram of the post-trained specimen subjected to four complete training cycle with 8% pre-strain and various constrained stress conditions: a) endothermic heat flow; and (b) exothermic heat flow.

results [253] showed that the shape recovery characteristics influenced by cold rolling or thermal cycling are similar because dislocations are imparted during these processes. Thus, the mechanism operating behind separation of *R*-phase and *M*-phase peaks in DSC is related to dislocations.

6.1.4 Summary

Figures 6.5(a) and (b) respectively summarize the changes in endothermic and exothermic transformation enthalpy, H , as a function of applied constrained stress and number of training cycles. Irrespective of the number of cycles, the figure shows the linear decrease of H with an increase of constrained stress. The value of H also showed a sign of further reduction when the number of training cycle increased to fourth cycle. The monotonous decrease of H with increasing deformation [33, 236, 252, 254] and further decrease of H due to cyclic effect were also observed in [97, 255].

As observed earlier in Chapter 4, the value of ε_{SATW} showed its peak at 200MPa. This corresponds to about 16J/g of endothermic H generated at $N = 1$, as indicated

CHAPTER 6. Thermodynamic Analysis

Figure 6.5 The characteristic of transformation enthalpy as a function of applied constrained stress and number of training cycles: a) endothermic ΔH ; and (b) exothermic ΔH .

by the dashed line in Figure 6.5(a). Incidentally, when considering the stress-free condition, the maximum ε_{TW} appeared at about 13% pre-strain [28, 33, 184], where at this strain level the ΔH was also found to be about 16J/g [33]. It is also noticed that, from the viewpoint of achieving maximum SATWME and TWME, an almost equal

Figure 6.6 The characteristics of DSC measured hysteresis width subjected to various degree of deformation and constrained stress conditions: *Stress-free curve depicts the Figure 11 in [28].

6.1 Analysis on Transformation Temperatures and Enthalpies

Figure 6.7 The characteristic of transformation enthalpy as a function of undergone constrained cycling and total martensite deformation progressed: a) endothermic H ; and (b) exothermic H .

amount of hysteresis width is generated at 13% deformation, as shown in Figure 6.6.

This effectively suggests a thermomechanical correlation between SATWME and TWME under full transformation condition.

The DSC measurements of endothermic and exothermic H in Test (2a) condition is summarized in Figure 6.7(a) and (b), respectively. For the cases of 50 and 400MPa, both endothermic and exothermic H decreases with increasing deformation. The endothermic H of 200MPa also decreases steadily with increasing deformation. The complication in exothermic H , however, is discernible in the 200 and 400MPa specimens, and it is related to the appearance of R -phase formation (Figure 6.3(d)). The abrupt decrease of endothermic H observed under 200MPa (10-12% deformation) and 400MPa (21-22% deformation) is likely attributed to the formation of internal stress field. It was observed [236] that increase in martensite pre-deformation increases the internal stress effect leading to the decrease of endothermic H .

The mechanism of transformation enthalpy in relation to thermodynamic energy balance equation will be further discussed in the next section.

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6.2 Thermodynamic Energy Balance Equations

The observed changes in transformation enthalpy measured via DSC for the post-trained specimens can be explained by considering the chemical and non-chemical energy contributions imparted from the thermomechanical treatment. In general, because of the presence of non-chemical free energies, G_{nch} , it is necessary to undercool below M_s -temperature and superheat above A_s -temperature to initiate the respective phase transformations. In so doing the chemical driving force, G_{ch} , overcomes the opposing non-chemical energies [95, 133, 204, 205, 256]. With reference to equation (6.1), G_{nch} consists of

$$\Delta G_{nch} = \Delta E_{el} + \Delta E_{fr} . \quad (6.2)$$

Following the work of Wollants et al. [208], the thermomechanical relation between G_{ch} and G_{nch} can be represented by the free energy-temperature-pressure (G - T - P) diagram, as illustrated in Figure 6.8. From the first and second law of thermodynamics, the chemical Gibbs free energy is related to its two independent variables pressure and temperature (P , T) by

$$G(P, T) = U + PV - TS = H - TS \quad (6.3)$$

where U is the internal energy, V is the volume, H and S are the enthalpy and entropy of the system, respectively. From equation (6.3), the fundamental equation is given by

$$dG = VdP - SdT . \quad (6.4)$$

6.2 Thermodynamic Energy Balance Equations

Figure 6.8 Schematic of Gibbs free energy change as a function of temperature T and pressure P .

Then, the thermodynamic equilibrium temperature is defined at T_0 by fixing the pressure at constant. On rearranging equation (6.4), the equilibrium values of P and T (where $dG/dT = 0$) are formulated as

$$\frac{dP}{dT} = \left(\frac{\Delta S}{\Delta V} \right) = \left(\frac{\Delta H}{T \Delta V} \right), \quad (6.5)$$

which is the generalized form of Clausius-Clapeyron equation. In Figure 6.8, with an increase of pressure ($P_0 \rightarrow P_1$) the T_0 shifts to a higher temperature T_0' . This will be accompanied by the increase of transformation temperatures M_s and A_s at which ΔG_{ch} overcomes the ΔG_{nch} to initiate the respective forward and reverse transformations. The free energy difference between chemical and non-chemical components leads to the generation of ΔG_{net} . After work of Ortin and Planes [95], T_0 can be formulated in

CHAPTER 6. Thermodynamic Analysis

relation to the frictional energy dissipated in each forward ($A \rightarrow M$) and reverse ($M \rightarrow A$) transformations (i.e. $E_{fr}^{A \rightarrow M}$ and $E_{fr}^{M \rightarrow A}$)

$$\frac{E_{fr}^{A \rightarrow M}}{E_{fr}^{M \rightarrow A}} = \frac{T_0 - T_M}{T_A - T_0} \quad (6.6)$$

where T_M and T_A are the temperatures at which the forward and reverse transformation take place, respectively. If under the assumption that the frictional energies arising from forward and reverse transformation are the same at T_M and T_A temperatures (i.e. $E_{fr}^{A \rightarrow M} = E_{fr}^{M \rightarrow A}$), then the following relation is obtained

$$T_0 = \frac{(T_M + T_A)}{2}. \quad (6.7)$$

For non-thermoelastic martensitic transformations, T_0 is defined by [257]

$$T_0 = \frac{(M_s + A_s)}{2} \quad (6.8)$$

For thermoelastic transformations, two equilibrium temperatures were suggested [133]: i) when chemical free energy of an ideal defect-free material (i.e. $\Delta G_{ch} = 0$), it is defined by

$$T_0 = \frac{(M_s + A_f)}{2}; \quad (6.9)$$

and ii) when $\Delta G_{ch} + \Delta G_{nch} = 0$, where ΔG_{nch} is essentially linked to the evolution of

6.2 Thermodynamic Energy Balance Equations

stored elastic strain energy and frictional energy dissipation, it is defined by

$$T_0' = \frac{(M_f + A_s)}{2}. \quad (6.10)$$

The concept of approximating equilibrium temperature under condition $\Delta G_{ch} + \Delta G_{nch} = 0$ is illustrated in Figure 6.9. When there is no creation of elastic strain energy (e.g. single crystal), it would require no superheating or undercooling so that initiation of transformation at A_s and M_s principally equals to their finish temperatures A_f and M_f (Figure 6.9(a)). Under such condition, equal and opposite frictional resistance would act upon propagating forward/reverse transformation, as denoted by blue and red arrows in the figure. The use of equation (6.10) provides good approximation to T_0' . In fact, the use of equation (6.9) is also valid since temperature hysteresis is attributed to frictional resistance only. The creation of elastic strain energy, however, gives rise to the slope during heating and cooling (Figure 6.9(b)). If the elastic strain energy stored during forward transformation is released without any loss in its subsequent reverse one (i.e. $\Delta M = \Delta A$), and if the frictional resistance acts equally for $A \leftrightarrow M$ transformation (i.e. $E_{fr}^{A \rightarrow M} = E_{fr}^{M \rightarrow A}$), then the use of equation (6.10) still provides good approximation to T_0' .

However, using the relation $E_{fr}^{A \rightarrow M} + E_{fr}^{M \rightarrow A} = Q_A - Q_M$ where Q_M and Q_A represents the total amount of heat released and absorbed, respectively, in the calorimetry measurement [95], it becomes apparent from the present results (Figure 6.10) that $E_{fr}^{A \rightarrow M} \neq E_{fr}^{M \rightarrow A}$ in most cases. In other words, there are two other possible situations where $E_{fr}^{A \rightarrow M} < E_{fr}^{M \rightarrow A}$, $\Delta M < \Delta A$ (Figure 6.9(c)) and $E_{fr}^{A \rightarrow M} > E_{fr}^{M \rightarrow A}$, $\Delta M >$

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Figure 6.9 Schematic illustrations of thermoelastic transformation (strain-temperature curves) showing various ways to estimate equilibrium temperature: (a) system is at a local balance when chemical and non-chemical contributions to the total Gibbs free energy are zero at T_0' , temperature hysteresis is attributed to frictional energy dissipation only; (b) temperature hysteresis cycle under presence of elastic strain energy (stored and released during forward and reverse transformation, respectively) and frictional energy dissipation; (c) less elastic strain energy is available to assist the reverse transformation (i.e. extra heating is required from T_{eq} to initiate and complete the reverse transformation), T_{eq} shifts to a lower temperature due to less frictional resistance from the forward transformation; and (d) creation of large elastic strain energy opposing the forward transformation (i.e. M_s increases) and promoting the reverse one (i.e. less heating is required from T_{eq} to initiate and complete the reverse transformation), T_{eq}' shifts to a higher temperature due to large frictional resistance from the forward transformation.

ΔA (Figure 6.9(d)). Figure 6.10 shows the effect of total strain deformation on the DSC measured transformation temperatures and intervals for the 50MPa post-trained specimen. Note that analysis is restricted to 50MPa because of *R*-phase formation in 200 and 400MPa conditions, which makes approximation of M_s difficult. Evidently, $\Delta M < \Delta A$ or $\Delta M > \Delta A$ occurs when subjected to thermomechanical deformation (except at near 6% strain where ΔM and ΔA coincides). Variety of changes also occurred for the transformation temperatures due to increased deformation. The

6.2 Thermodynamic Energy Balance Equations

Figure 6.10 The characteristic of DSC measured transformation temperatures and intervals as a function of undergone 50MPa constrained cycling and various degrees of total martensite deformation: a) transformation temperatures, M_s , M_f , A_s and A_f ; and (b) transformation temperature intervals ΔM and ΔA .

thermodynamic mechanism operating behind such changes in temperature will be discussed further in the next section.

At this point, it is to be emphasized that frictional resistance to interfacial motion influences the hysteresis width [24]. This frictional resistance, E_{fr} , is interrelated to the creation of elastic strain energy (reflected by the temperature intervals ΔM and ΔA), since contribution of elastic strain energy opposes the forward transformation and promotes the subsequent reverse one (i.e. M_s and A_s decreases). Thus, to account for the frictional energy difference between forward and reverse transformation, correlating $E_{fr}^{A \rightarrow M} / E_{fr}^{M \rightarrow A}$ to $\Delta M / \Delta A$ in equation (6.6) makes the approximation of T_0' more precise as to capture the thermoelastic phenomena (Figures 6.9(c) and (d)). The equilibrium temperature T_{eq} is thus given by

$$T_{eq} = \frac{\Delta A M_f + \Delta M A_s}{\Delta A + \Delta M}. \quad (6.11)$$

T_{eq} from equation (6.11) will be used to estimate the transformation entropy, ΔS .

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Following the work of Wollants et al. [208], ΔS is given by (under assumption that influence of heat capacity difference on the system is small, i.e. $\Delta C_p = 0$)

$$\Delta S^{\text{system}} = \Delta S_{T_{eq}}^{A \rightarrow M} = \frac{\Delta H_{T_{eq}}^{A \rightarrow M}}{T_{eq}} \quad (6.12)$$

and entropy difference in other direction of transformation equals

$$\Delta S_{T_{eq}}^{M \rightarrow A} = \frac{\Delta H_{T_{eq}}^{M \rightarrow A}}{T_{eq}}, \quad (6.13)$$

which is further utilized to estimate the E_{fr} and elastic strain energy (quantified in terms of transformation enthalpy ΔH_{el}), given by

$$E_{fr}^{A \rightarrow M} = \Delta S_{T_{eq}}^{A \rightarrow M} (M_f - T_{eq}) \quad (6.14)$$

for the forward transformation, and the reverse one is given by

$$E_{fr}^{M \rightarrow A} = \Delta S_{T_{eq}}^{M \rightarrow A} (A_s - T_{eq}). \quad (6.15)$$

The maximum ΔH_{el} stored during forward transformation is given by

$$\Delta H_{el}^{A \rightarrow M} = \frac{\Delta M \times \Delta S_{T_{eq}}^{A \rightarrow M}}{2} \quad (6.16)$$

and the release of ΔH_{el} during reverse transformation is given by

6.2 Thermodynamic Energy Balance Equations

$$\Delta H_{el}^{M \rightarrow A} = \frac{\Delta A \times \Delta S_{T_{eq}}^{M \rightarrow A}}{2} \quad (6.17)$$

In this way, the observed decreases in ΔH from the DSC results (Figures 6.5 and 6.7) will be explained by quantifying those non-chemical components (E_{fr} and ΔH_{el}) via equations (6.14-6.17), and relating them to the thermodynamic transformation enthalpy formulations.

6.3 Transformation Enthalpy Formulations

In the case of Test (1a) and (3a), both the endothermic and exothermic transformation enthalpy showed a strong monotonic decrease with increasing applied constraint stress and number of training cycles (Figure 6.5). Previous studies pointed out [97, 202] that this is because elastic strain energy has been predominant over irreversible frictional work in lowering the net enthalpy, H_{net} , as measured by calorimetry. During the forward $A \rightarrow M$ transformation (exothermic), H_{net} is governed by the thermodynamic balance equation [95]:

$$-\Delta H_{net}^{A \rightarrow M} = -\Delta H_{ch}^{A \rightarrow M} + \Delta H_{el}^{A \rightarrow M} + E_{fr}^{A \rightarrow M} \quad (6.18)$$

where $\Delta H_{ch}^{A \rightarrow M}$ represents the chemical enthalpy and $\Delta H_{el}^{A \rightarrow M}$ is the elastic enthalpy stored as elastic strain energy. All the enthalpy terms given in equation (6.18) are considered in absolute values. Likewise, during the reverse $M \rightarrow A$ transformation (endothermic) is governed by the thermodynamic balance equation:

$$\Delta H_{net}^{M \rightarrow A} = +\Delta H_{ch}^{M \rightarrow A} - \Delta H_{el}^{M \rightarrow A} + E_{fr}^{M \rightarrow A}. \quad (6.19)$$

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Here, the sign convention of the net and chemical transformation has been given as *positive* in equation (6.19) and as *negative* in equation (6.18), since the heat is absorbed and dissipated during the respective reverse and forward transformations. It is apparent from equations (6.18) and (6.19) that only the term H_{el} can simultaneously reduce the net transformation enthalpy, assuming that the chemical transformation enthalpy (in absolute value) remains identical during forward/reverse transformations. Nevertheless, basing on the study of Salzbrenner and Cohen [134], H_{el} and E_{fr} amounts to about 3.5 and 1.2J/g, respectively (assuming that H_{ch} is approximated from the as-annealed specimen, *see* Figure A.2). Obviously, these values do not suffice to account for the observed decreases in H_{net} and thus requires an additional term. In this respect, Mari and Dunand [97] included the transformation enthalpy arising from defects such as dislocations, H_d , to reinterpret the thermodynamic balance formulations as

$$-\Delta H_{net}^{A \rightarrow M} = -\Delta H_{ch}^{A \rightarrow M} + \Delta H_{el}^{A \rightarrow M} + \Delta H_d^{A \rightarrow M} + E_{fr}^{A \rightarrow M} \quad (6.20)$$

and

$$\Delta H_{net}^{M \rightarrow A} = +\Delta H_{ch}^{M \rightarrow A} - \Delta H_{el}^{M \rightarrow A} + \Delta H_d^{M \rightarrow A} + E_{fr}^{M \rightarrow A}. \quad (6.21)$$

However, based on the fact that dislocation mobility in austenite phase is higher than in the martensite phase [258] which makes it easier for dislocations to rearrange themselves during reverse transformation, and that defect recovery can lead to a decrease of $\Delta H_{net}^{M \rightarrow A}$ [202], the sign convention of $\Delta H_d^{M \rightarrow A}$ in equation (6.21) should read

$$\Delta H_{net}^{M \rightarrow A} = +\Delta H_{ch}^{M \rightarrow A} - \Delta H_{el}^{M \rightarrow A} - \Delta H_d^{M \rightarrow A} + E_{fr}^{M \rightarrow A} \quad (6.22)$$

6.3 Transformation Enthalpy Formulations

Finally, based on the transformation enthalpy formulations (equations (6.19 and 6.21)) and those put forward earlier (equations (6.14-6.17)), non-chemical components contributing individually to the decrease of ΔH_{net} were quantified. The results are shown in Tables 6.1 and 6.2 for the Test (1a) and (3a) conditions, and shown in Figure 6.11 for the Test (2a) condition. As mentioned earlier in Section 6.2, ΔH analysis is restricted to those DSC results containing no R -phase formation, i.e. the presence of R -phase in the exothermic curve makes approximation of M_s difficult, leading to inaccurate estimation of ΔM and causes further inaccuracy in the estimate of T_0 , ΔS , E_{fr} and ΔH_{el} .

Applied constraint stress (MPa)	No. of training cycles (N)	* ΔH_{net} (J/g)	* ΔH_{ch} (J/g)	T_{eq} (K)	ΔS (J/gK)	* ΔH_{el} (J/g)	* ΔH_{d} (J/g)	E_{fr} (J/g)
20	1	19.3	22.6	325.6	0.059	0.32	2.04	0.94
100	1	18.1	22.6	324.8	0.056	0.61	2.56	1.33
50	4	18.2	22.6	323.7	0.056	0.54	2.72	1.14

*Given in absolute values.

Table 6.1 The DSC measured net transformation enthalpy ΔH_{net} and chemical enthalpy ΔH_{ch} (as-annealed specimen), calculated phase equilibrium temperature T_{eq} (equation (6.11)) and transformation entropy ΔS (equation (6.12)), estimated stored elastic strain energy ΔH_{el} (equation (6.16)), defect ΔH_{d} (equation (6.20)) and frictional energy dissipation E_{fr} (equation (6.14)) for $A \rightarrow M$ transformation.

Applied constraint stress (MPa)	No. of training cycles (N)	* ΔH_{net} (J/g)	* ΔH_{ch} (J/g)	T_{eq} (K)	ΔS (J/gK)	* ΔH_{el} (J/g)	* ΔH_{d} (J/g)	E_{fr} (J/g)
20	1	18.7	23.1	325.6	0.057	0.32	5.01	0.93
100	1	17.5	23.1	324.8	0.054	0.33	5.98	0.71
50	4	17.3	23.1	323.7	0.053	0.35	6.20	0.75

*Given in absolute values.

Table 6.2 The DSC measured net transformation enthalpy ΔH_{net} and chemical enthalpy ΔH_{ch} (as-annealed specimen), calculated phase equilibrium temperature T_{eq} (equation (6.11)) and transformation entropy ΔS (equation (6.13)), estimated stored elastic strain energy ΔH_{el} (equation (6.17)), defect ΔH_{d} (equation (6.22)) and frictional energy dissipation E_{fr} (equation (6.15)) for $M \rightarrow A$ transformation.

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Based on these results (Tables 6.1 and 6.2, Figure 6.11), for $A \rightarrow M$ forward transformation, the main effect of increase in applied constraint stress is to increase all the non-chemical energy terms ΔH_{el} , ΔH_{d} and E_{fr} . Despite the low applied stress of 50MPa, increase in number of training cycle also results in the prominent increase of ΔH_{d} , indicating that defects accumulate with successive cycling. These defects obstruct $A \rightarrow M$ interphase movement during transformation, leading to the increased strain and frictional energies. Furthermore, the values of ΔH_{el} and E_{fr} have increased to their maximum at 10% deformation and decrease with further deformation, while the ΔH_{d} increased continuously with increasing deformation, as shown in Figure 6.11. The decrease of ΔH_{el} after 10% deformation is likely related to the internal stress formed by the defects σ_{ij}^d : the elastic strain energy associated with defects ΔE_e^d is represented by [225, 255]

$$\Delta E_e^d = -\frac{1}{\rho} \int \sigma_{ij}^d \varepsilon_{ij}^d dV / V \quad (6.23)$$

where ρ is the density, ε_{ij}^d is the transformation strain, and V is the volume of the specimen. The ΔE_e^d can be treated as either positive or negative quantity depending on the nature of σ_{ij}^d . Previous study demonstrated [203] that relaxation of internal stress due to grain growth decreases ΔH_{el} . Likewise in the present study, the observed decrease in internal stress (Figure 4.27) is thus connected to the decrease in ΔH_{el} . As a consequence of ΔH_{el} dissipation, there will be less obstruction to the forward transformation, thus further transformation requires less under-cooling (i.e. M_{f} increases to higher temperature and E_{fr} decreases).

6.3 Transformation Enthalpy Formulations

Figure 6.11 The estimated non-chemical energy components for the specimen undergone 50MPa cycling with various degrees of deformation: (a) elastic strain energy and frictional energy dissipation for the $A \rightarrow M$ and $M \rightarrow A$ transformation; and (b) transformation enthalpy arising from defects.

For $M \rightarrow A$ reverse transformation, on the other hand, it can be seen that the value of ΔH_d tends to be significantly larger than that of those detected under $A \rightarrow M$ transformation. This indicates that during the reverse transformation, some of the defect structures vanish due to rearrangement and reduces the amount of energy dissipated for ΔH_{el} and E_{fr} .

Based on the observations made thus far, it can be concluded that a predominant mechanism leading to decrease in ΔH_{net} in both directions of $M \leftrightarrow A$ transformation is the defects imparted through thermomechanical treatment. It is also noteworthy to point out that, contrasted to a general belief [95, 225] the mechanisms of storing and releasing of elastic strain energy and consuming of frictional energy as heat are not necessarily equal during $M \rightarrow A$ and $A \rightarrow M$ transformation.

6.4 Further Remarks and Summary

Thermodynamic analysis on the DSC results was presented in this chapter. The thermomechanical correlation between the development mechanisms of SATWME and TWME was demonstrated by the transformation enthalpy, H , and temperature

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hysteresis width measurements. Under fully transformed condition, both memory effects showed strong correlation at their maximum, but did not project the same mechanisms below and above the maximum level.

The formation of intermediate *R*-phase was confirmed by the XRD measurement. *R*-phase appeared in the exothermic curve after subjected to higher constrained stress cycling namely 200, 300 and 400MPa. The separation of the two peaks M_p and R_p became pronounced with increasing magnitude of applied constrained stress. It is due to increased density of dislocations.

The conventional way of estimating equilibrium temperature was revised by incorporating the difference in elastic strain energy stored and released during forward and reverse transformation, respectively. It was found that the defects imparted through thermomechanical treatment were the main cause for the decrease in DSC measured ΔH .

CHAPTER 7

Mechanism of Two-step Transformation

The results presented in Chapter 5 have shown that the two-step reverse transformation can be generated by means of imposing one-off partial transformation between austenite start and finish temperatures. In the course of reverse transformation, the fraction of detwinned/reoriented martensites is deliberately retained under constraint. The systematic investigation of strain-temperature curves have shown that the development of SATWME and TWME are largely influenced by the mechanism of two-step transformation that is tightly connected to the progress in martensite deformation, rearrangement of dislocations and martensite variant re-configurations.

In this chapter, attempts were made to understand the above interrelated micro-mechanisms more comprehensively by adopting macromechanical and thermodynamical approaches:

- i) Strain comparison of the partially transformed strains measured in the first heating cycle and the two-step recovery strains in the next cycle, described in Section 7.1; and
- ii) Strain-temperature and calorimetry analysis incorporating the creation and relaxation mechanism of elastic strain energy into the pre-positioning and

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overheating phenomena of the two-step reverse transformation, respectively, described in Section 7.2.

- iii) Based on the findings in i) and ii), and on the dislocation pile-up theory, a two-step transformation model will be proposed in Section 7.3.

7.1 Strain Comparison

As has been briefly discussed in Chapters 1 and 2, the influence of retained martensite on the recovery strain on one hand is claimed to improve the TWME by increasing the amount of retained martensite during training [58]. On the other hand, the retention of martensite caused by the locking mechanism of dislocations has been claimed to decrease the amount of recoverable strain [51]. Also works by Stalmans et al. [60, 61] considered the effect of martensite remnants on TWME to be insignificant since these remnants can be wiped out completely once overheated above A_f -temperature. The present research so far has demonstrated that the as-annealed NiTi specimen undergoing partial reverse transformation results in the retention of detwinned/reoriented martensite, causing significant changes in the strain-temperature response of the SATWME and TWME.

The above changes in two-way memory effects can be explained from the viewpoint of internal plastic deformation caused by the accommodation process of distinctively oriented martensite variants, namely stress-assisted martensite (SAM) and detwinned/reoriented martensite. In essence, SAM is produced as a result of stress-assisted martensitic transformation evoked during 1st cooling (name it collectively as primary transformed martensite, PRT- M), whereas the latter martensite refers to those untransformed oriented martensite variants (name it collectively as originally transformable martensite, ORT- M).

Figure 7.1 Example of strain-temperature curves generated due to 18% pre-strain and 200MPa constrained cycling: (a) 1st heating and cooling; and (b) 2nd heating, unloading and stress-free 2nd cooling and 3rd heating.

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Figure 7.1(a) shows the example of partial reverse transformation imposed between A_s and A_f during 1st heating and the designation of *ORT-M* and *PRT-M*. Figure 7.1(b) shows the subsequent transformation phenomena including the emergence of two-step transformation and the development of TWME upon release of constrained stress. For an ease of comparison, all the strain-temperature curves shown in Figure 7.1(b) have been normalized to zero strain at the completion of unloading. The orientation mismatch among *ORT-M* and *PRT-M* is inevitable and for this reason, internal plastic deformation builds up. Note, however, that in the case of Test (3b) where repeated constrained cycles were applied, the orientation mismatch arises also from the retransforming *PRT-M* and the retained *PRT-M*.

To support the argument put forward on internal plastic deformation further, the comparison of various strains were made, firstly between the partially transformed strain, ε_{PT} , and the strain generated during the first-half of reverse transformation, ε_{R1} . Secondly, between the untransformed strain, ε_{RM} , and the strain generated during the second-half of reverse transformation, ε_{R2} .

7.1.1 Fixed Pre-strain with Variable Constrained Stress Condition

Figure 7.2(a) shows the strain comparison plot for the case of 4% pre-strain with 50MPa constrained stress condition. It can be seen that both ε_{R1} and ε_{R2} curves stayed in close proximity with their respective reference curves namely ε_{PT} and ε_{RM} with increasing amount of retained martensite, %RM. The ε_{R2} curve also coincided extremely well with the ε_{RM} curve for the cases of 200 and 350MPa, as shown in Figure 7.2(b) and (c), respectively. This indicates a fact that the second-half of reverse transformation taking place between A_s and A_f temperature during 2nd heating is

7.1 Strain Comparison

Figure 7.2 Strain comparison plot for the case of 4% pre-strain with variable constrained stress conditions.

attributed to $ORT-M$ transforming into austenite, during which its recovery strain magnitude is unaffected by the partial transformation. Based on this indication, it can be suggested further that the first-half of reverse transformation taking place between A_s' and A_f' is derived by the sequence of transformations: $ORT-M \rightarrow A \rightarrow PRT-M \rightarrow A$. Thus, the $PRT-M$ and $ORT-M$ transforms into A sequentially in the order of increasing temperature during 2nd heating. A similar sequential transformation due to partial transformation was also observed in the previous DSC measurements [71-73, 75].

The evidence of insignificant difference observed between ϵ_{R1} and ϵ_{PT} under 50MPa implies that the SATWME is insensitive to partial transformation. This

CHAPTER 7. Mechanism of Two-step Transformation

implication can be elaborated further as follows: considering that the martensite pre-deformation process was terminated in the midst of partial detwinning region (Figure 5.1) and that applied constrained stress was relatively weak in directing the growth of martensite variants, the amount of PRT- M generated is said to be only marginal. In contrast, the amount of PRT- M could multiply with increasing magnitude of constrained stress and hence the value of ε_{R1} gets larger than that of ε_{PT} when subjected to 200 and 350MPa (Figure 7.2(b) and (c)). These PRT- M variants are required to accommodate themselves with the neighboring ORT- M variants in the 1st cooling following the 1st heating of partial reverse transformation. Owing much to an orientation mismatch among ORT- M and PRT- M variants, internal plastic deformation occurs (as in a form of mismatched boundary, shown in Figure 5.16). Due to such plastic deformation, it deprives PRT- M of transforming into austenite and lowers the overall magnitude of SATWME.

It should be emphasized that, for the case of 50MPa, associated not only with the negligible changes in martensitic strain (Figure 5.2(b)) but also with the localized nature of martensite deformation (i.e. only some area of ORT- M variants retransform into PRT- M after 4% pre-strain and constrained thermal cycling), only some fraction of the affected PRT- M variants has potentially lowered the SATWME. For these reasons, the detrimental effect of partial transformation on the SATWME is alleviated under 50MPa constrained thermal cycling.

7.1.2 Fixed Constrained Stress with Variable Pre-strain Condition

On further exploring the mechanism of two-step transformation, Figure 7.3 shows the strain comparison plot for the cases of variable pre-strain (8, 13, 18 and 23%) with fixed 200MPa constrained stress condition. A similar trend to what was observed

7.1 Strain Comparison

Figure 7.3 Strain comparison plot for the case of 8-23% variable pre-strains with 200MPa constrained stress condition.

earlier in Figure 7.2, the ϵ_{R2} curve closely overlapped on the ϵ_{RM} curve, irrespective of the magnitude of pre-strain applied. This evidence revalidates the interpretation of an order of two-step reverse transformation put forward earlier: PRT-*M* and ORT-*M* transforms into austenite sequentially in the order of increasing temperature. In the first-half of reverse transformation, it is apparent that the shape recovery displayed in ϵ_{R1} decreases somewhat nonlinearly with increasing %RM. Moreover, there is a clear tendency that this decrease of ϵ_{R1} becomes more nonlinearly defined and shows acute decrease at low %RM range for the higher pre-strained conditions (Figures 7.3(c) and (d)). The acute decrease effectively indicates the generation of high degree of internal plastic deformation.

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Given that the ε_{R2} curve was virtually unaffected by the partial transformation, the decreasing trend observed earlier in ε_{SATW} curves (Figure 5.14) are thus predominantly characterized by the ε_{R1} curve.

7.1.3 Repeated Cyclic Condition

With reference to Figure 5.19 presented in Chapter 5, the strain comparison was made for those cyclic conditions: iii) partial transformation at 1st and 3rd heating; and iv) partial transformation at 4th heating. The results are summarized in Table 7.1. Note that, in view of strain comparison, the result obtained for cyclic condition ii) practically overlaps with that for the condition iii), hence it is omitted from the table.

Cyclic condition:		ε_{PT} (%)	ε_{R1} (%)	ε_{RM} (%)	ε_{R2} (%)	Remark:
i) Full transformation at	1 st heating	2.41	N/A	N/A	N/A	Benchmark for extrapolating the %RM.
	2 nd heating	4.86				
	3 rd heating	5.40				
	4 th heating	5.69				
	5 th heating	5.95				
iii) Partial transformation at	1 st heating	1.38	1.88	1.03	1.19	43%RM, ($\varepsilon_{R1} > \varepsilon_{PT}$)
	3 rd heating	4.17	3.43	1.23	0.93	23%RM, ($\varepsilon_{R1} < \varepsilon_{PT}$)
iv) Partial transformation at	4 th heating	3.45	2.46	2.24	2.14	40%RM, ($\varepsilon_{R1} < \varepsilon_{PT}$)

Table 7.1 Strain comparison of ε_{R1} and ε_{PT} , ε_{R2} and ε_{RM} in the first and second-half of reverse transformation, respectively, under various cyclic conditions.

Focusing on the result of cyclic condition iii), there is a clear transition for the strain relation ($\varepsilon_{R1} > \varepsilon_{PT}$) established at early cycle changing to its complete opposite relation ($\varepsilon_{R1} < \varepsilon_{PT}$) at later cycle. Also, it is observed that when the partial

7.1 Strain Comparison

transformation was imposed at 4th heating, the strain relation ($\varepsilon_{R1} < \varepsilon_{PT}$) persists. The occurrence of such transition can be explained from the viewpoint of martensitic strain, ε_{MA} . With reference to Figure 5.19(c), it is noticed that the value of ε_{MA} reaches about 10% upon completion of 1st cycle. Obviously, this reflects the shape recovery behavior observed for the 4% pre-strain with 200MPa cycling; its strain comparison plot shown in Figure 7.2(b) reveals that the strain relation ($\varepsilon_{R1} > \varepsilon_{PT}$) hold true at 43%RM. However, by the time next partial transformation takes place at 3rd heating the value of ε_{MA} reaches 14% level, meaning that the strain comparison plot used earlier becomes no longer valid. The same reasoning is applicable to the case of cyclic condition iv), where the value of ε_{MA} reaches about 19% at the end of 4th cooling.

Thus, basing on the strain comparison results obtained from Figure 7.3 and Table 7.1, the prevalence of strain relation ($\varepsilon_{R1} < \varepsilon_{PT}$) occurs at low %RM range with increasing magnitude of either applied pre-strain or ε_{MA} . It also means that similar to what we had discovered earlier for the fully transformed condition, the direct application of pre-strain and cyclically progressed ε_{MA} plays mutual role in determining the ε_{SATW} , even in the case of partial transformation.

7.1.4 Equal Strain Position (ESP) Analysis

The effects of decrease in ε_{R1} on the development mechanism of TWME are discussed in this section. In Chapter 5, it has been proposed that the magnitude of TWME depend on the dislocation structures imparted by training. This is owing to a characteristic arrangement of dislocations and the density of dislocations produced thereby [259, 260]. In fact, the aligned dislocations distributed uniformly inside martensite are regarded as the main characteristic feature of a trained specimen

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exhibiting TWME [261]. It is proposed by the present author that the introduction of retained martensite during training disrupts this aligned dislocations arrangement to be heterogeneous and causes detrimental effect on the TWME.

To what extent the presence of disrupted dislocations impinge on the TWME is being investigated by observing the shift of so-called “*equal strain position*,” ESP , and its related phenomena. The term ESP is defined by $ESP = ESP_f - ESP_i$ and its amount of shift and direction are denoted by the bold dashed line with a closed arrow-head in Figures 7.2 and 7.3. To be noted is that the initial equal strain position, ESP_i , is determined by the intersection of ε_{PT} and ε_{RM} curves, i.e. the ESP_i is located at near 50%RM. The symbol ε_i has been assigned to represent the strain level at ESP_i . In the same way, the final equal strain position, ESP_f , is determined by the intersection of ε_{R1} and ε_{R2} curves, and its associated strain level is the ε_f . Thus, the shift of equal strain position will be accompanied by the shift of strain level, $\Delta\varepsilon = \varepsilon_f - \varepsilon_i$.

Tables 7.2 and 7.3 summarize the quantification of these equal strain positions with corresponding strain levels measured from Figure 7.2 and 7.3, respectively. It becomes apparent that the ESP_i shifts to a new position ESP_f after undergoing partial transformation. It is caused by the decreasing trend in ε_{R1} . As indicated by the positive value of ESP , applying high constrained stress tends to make PRT- M dominant in the two-step reverse transformation. That is, the amount of recovery in ε_{SATW} is dominated by the PRT- M variants transforming into austenite. Associated with the value of ESP , the dominance of PRT- M causes the $\Delta\varepsilon$ to be increased, though its increment is not directly proportional to the ESP .

On the contrary, increasing pre-strain magnitude and thermal cycling under 200MPa results in the opposite tendency; it becomes ORT- M dominant after 13% pre-

7.1 Strain Comparison

σ (MPa)	ESP_i (%)	ESP_f (%)	ΔESP (%)	ε_i (%)	ε_f (%)	$\Delta \varepsilon$ (%)	Remark:
50	50.1	42.9	-7.2	1.01	0.99	-0.02	ORT- <i>M</i> dominant
200	50.0	59.0	+9.0	1.24	1.48	+0.24	PRT- <i>M</i> dominant
350	50.0	91.1	+41.1	0.36	0.55	+0.19	Extremely PRT- <i>M</i> dominant

Table 7.2 The shift of equal strain position for the case of 4% pre-strain with variable constrained stress condition.

Pre- ε (%)	ESP_i (%)	ESP_f (%)	ΔESP (%)	ε_i (%)	ε_f (%)	$\Delta \varepsilon$ (%)	Remark:
8	50.3	60.1	+9.8	1.32	1.49	+0.17	PRT- <i>M</i> dominant
13	50.3	45.4	-4.9	1.52	1.40	-0.12	ORT- <i>M</i> dominant
18	49.6	44.6	-5.0	1.15	1.02	-0.13	ORT- <i>M</i> dominant
23	49.7	46.5	-3.2	0.78	0.66	-0.12	ORT- <i>M</i> dominant, ΔESP stabilizes

Table 7.3 The shift of equal strain position for the case of 8-23% pre-strain with 200MPa constrained stress condition.

strain. This tendency is reflected by the negative value of ESP in Table 7.3. A similar result is also evident under 50MPa. Meanwhile, it is observed that further pre-straining to 23% under 200MPa results in the stabilization of ESP .

At this point, one may recognize that the observed shift of ESP arises from the following ramification: the nucleation of stress-assisted martensite (i.e. refers to PRT-*M* in the present case) tends to depend on the same sites and embryos [262]. Furthermore, it is known that constrained thermal cycling tends to favor the growth of selected variants in expense of others [34]. Thus, PRT-*M* variants persist on nucleating at their preferred sites without having to annihilate the nucleation sites provided for the ORT-*M* during the 1st cooling. Clearly, this persistence of nucleating PRT-*M* is reflected by the ESP_f shifting to a higher %RM level and is observed to be particularly prominent for the case of 350MPa. This phenomenon occurs due to the

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fact that greater the magnitude of constrained stress the larger is the volume fraction of stress-assisted martensite produced [24]. In this respect, the opposite scenario of ESP_f shifting to a lower %RM could indicate the arrest of PRT- M persistence over ORT- M .

As for the case of cyclic condition, the persistence of nucleating freshly transformed PRT- M over retained PRT- M seems to follow the relation displayed in PRT- M versus ORT- M , e.g. for the cyclic condition iv), it is apparent that the value of ε_{R1} is higher than ε_{R2} and their difference is only marginal at 40%RM (Table 7.1). Considering the fact that the value of ε_{MA} had reached about 19% at the end of 4th cooling, the observed relation of ε_{R1} and ε_{R2} corresponds well with the strain comparison plot shown in Figure 7.3(c).

It is then anticipated that heterogeneous dislocations will be formed in the microstructure when ORT- M and PRT- M variants try to coordinate with each other. As in the case of cyclic condition, the variant coordination takes place between freshly transformed PRT- M and retained PRT- M . Work by Gilemany and Gil [242], they relate pronounced microstructural anisotropy in the polycrystalline shape memory alloy to the increased temperature interval, $\Delta M = M_s - M_f$. Indeed, as shown in Figure 7.1, there is a clear tendency that the original slope in the 1st cooling gets inclined at an angle (modified slope) after experiencing partial transformation. The results presented so far (Figures 5.3(a), 5.4(a) and 5.12(a), (c)) further show that larger the fraction of martensite retained in the 1st heating the more pronounced the shallow inclination of strain-temperature curve in the subsequent 1st cooling. This indicates the evolution of stored elastic strain energy, increase in irreversible energy and prolonged undercooling, ΔM .

7.1 Strain Comparison

As a general trend, evolution of stored elastic strain energy promotes the reverse transformation in such a way as to decrease the A_s -temperature of the next reverse transformation. Meanwhile an increase in irreversible energy give rise to increased frictional resistance against interfacial motion. This increased irreversible energy appears to be imposed on the development process of TWME. The slope of strain-temperature hysteresis modifies greatly depending on the magnitudes of applied pre-strain and constrained stress, and the amount of retained martensite. In this regard, it is possible to deduce higher degree of disrupted dislocations being produced for the ones with severely modified strain-temperature hysteresis.

Figure 7.4(a) depicts the case of 4% pre-strain with 200MPa constrained cycling and partially transformed to near 50%RM. Undergoing partial transformation entails the modification of strain-temperature response in the 1st cooling, which results in the prolonged undercooling, M . The stored elastic strain energy is then released in the 2nd heating, whereby promotion of the first-half of reverse transformation takes place. Based on M , a higher storage and relaxation of elastic strain energy can occur when higher magnitude of pre-strain is applied, as depicted in Figure 7.4(b). The striking difference between the two cases arises because of the preponderance of internal forward and back stresses. A dominance of internal forward stress promotes the rearrangement of microstructures. Thus, the dislocations can move easily in the direction of forward transformation and the M reduces in the course of developing TWME (Figure 7.4(b)). In contrast, the weakening of internal forward stress retains large debris of irreversible energy from the disrupted dislocations, resulting in an increased M followed by a modification of strain-temperature hysteresis of TWME (Figure 7.4(a)).

In this way, following the same thought that disorderly distributed dislocations

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Figure 7.4 Example of strain-temperature curves generated due to: (a) 4% pre-strain, 200MPa constrained cycling and partially transformed to 52%RM; and (b) 18% pre-strain, 200MPa constrained cycling and partially transformed to 55%RM. Open dashed arrow indicates the degree of slope changes due to partial transformation (exaggerated).

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promote the removal of martensite variant participating in the spontaneous shape recovery [263], the magnitude of TWME decreases.

The creation and relaxation mechanism of elastic strain energy, in terms of pre-positioning and overheating phenomena of the first-half and second-half of reverse transformation, respectively, will be further discussed in the next section.

7.2 Creation and Relaxation Mechanism of Elastic Strain Energy

To gain further understanding on the mechanism of the two-step reverse transformation, a quantitative evaluation of the elastic strain energy is presented in this section. The evaluations are twofold: i) the thermomechanical relationship between the creation of elastic strain energy and the pre-positioning of the first-half of reverse transformation, measured in terms of $A_s = [A_s^1(1^{\text{st}} \text{ heating}) - A_s'(2^{\text{nd}} \text{ heating})]$; and ii) the relationship between the relaxation of elastic strain energy and the amount of overheating, measured in terms of $A_s - T_H = [A_s(2^{\text{nd}} \text{ heating}) - T_H(1^{\text{st}} \text{ heating})]$. Recall that T_H represents the target temperature at which partial reverse transformation was imposed (cf. Figure 3.7(a)).

In addition, the evaluations i) and ii) are cross-examined by the DSC results of incomplete transformation-induced two-step reverse transformation.

7.2.1 Strain-Temperature Analysis

It has been well established to interpret the observed changes of A_s -temperature as being caused by the applied external stress and stored elastic strain energy [95, 133, 199]. Results of present study (Figures 5.2-5.4, 5.12 and 5.19) reveal that the process of storing elastic strain energy under constraint was reflected by the slope of the 1st

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cooling path. By the same token, the relaxation of the stored elastic energy was reflected by the slope of the 2nd heating path.

With an aim to capture such changes in the slope, four results of the strain-temperature curves subjected to near 50%RM were selected from Figures 5.2-5.4 and 5.12. The selected results are arranged in Figure 7.5 with respect to the order of increasing magnitude of constrained stress (a)-(c) and pre-strain (d).

From Figure 7.5(a)-(c), there is a clear trend in the storage and relaxation of elastic strain energy that the values of A_s and A_s-T_H both increases with increasing magnitude of constrained stress (note that for the case of 50MPa, the value of A_s was unable to detect since its 1st heating had involved with two-step reverse transformation). Comparing Figure 7.5(b) and (d), further increase in the magnitude of pre-strain to 13% also resulted in the increase of A_s (i.e. $52 \rightarrow 71^\circ\text{C}$), but on the

Figure 7.5 The comparison of strain-temperature curves generated at near 50%RM.

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contrary it showed the decrease of A_s-T_H (i.e. $6 \rightarrow 3^\circ\text{C}$).

Figure 7.6(a) and (b) respectively summarizes the characteristic of A_s as a function of retained martensite, %RM, with various magnitudes of constrained stress and pre-strain. It is seen from the figures that the value of A_s tend to rise continuously with increasing %RM. Associated with this promoted increase of reverse transformation temperature, the value of A_s-T_H decreases with increasing %RM, as shown in Figure 7.7. Important to note is that while observing the abrupt decrease of A_s-T_H in the low %RM range, the 50MPa and the 200MPa (23% pre-strain) curves showed peculiar increase after exceeding 50%RM. This peculiar phenomenon

Figure 7.6 The degree of pre-positioning process in the first-half of reverse transformation, A_s , analyzed as a function of fraction of retained martensite and thermomechanical treatment conditions: (a) variable constrained stress; and (b) variable pre-strain with 200MPa cycling.

Figure 7.7 The degree of overheating process in the second-half of reverse transformation, A_s-T_H , analyzed as a function of fraction of retained martensite and thermomechanical treatment conditions: (a) variable constrained stress; and (b) variable pre-strain with 200MPa cycling.

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corresponds well with the decrease of M_s -temperature (Figures 5.8 and 5.18). Thus, it is connected to the development mechanism of internal back stress. Also to note is that for the case of 350MPa, the values of A_s and A_s-T_H in the low %RM range were not given in Figures 7.6 and 7.7 because of the degeneration feature of two-step reverse transformation (*see* Chapter 5, Section 5.1.4). For the same reason, the evaluation on the first-half and second-half of reverse transformation temperature intervals (A_s^1 and A_s^2), which will be described in the next section are omitted for the 350MPa subjected to 6 and 11%RM.

Returning to the comparison of Figure 7.5(b) and (d), it becomes apparent that the mechanism pertinent to the increase of A_s is accompanied by the shallow slope of the 1st cooling and first-half of 2nd heating paths, while the decrease of A_s-T_H is accompanied by the steep slope of the second-half of 2nd heating path. The clear evidence of generating two differently inclined slopes suggests a possibility for PRT- M and ORT- M to possess different relaxation mechanism of elastic strain energies. In general, elastic strain energy, ΔE_e , is created due to an elastic and inelastic accommodation of the transformational shape and volume changes:

$$\Delta E_e = \Delta E_e^s + \Delta E_e^t + \Delta E_e^d. \quad (7.1)$$

The first component appearing immediately on the right hand side is the elastic accommodation of strain energy ΔE_e^s , expressed as [225]

$$\Delta E_e^s = -\frac{1}{\rho} \int \sigma_{ij} \varepsilon_{ij}^t dV / V \quad (7.2)$$

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where ρ is the density, σ_{ij} is the applied stress, ε_{ij}^t is the transformation strain, and V is the volume of the specimen. The remaining two components are the strain energies associated with the internal stress field created due to the transformation σ_{ij}^t and associated with defects σ_{ij}^d , expressed respectively as [225]

$$\Delta E_e^t = -\frac{1}{2\rho} \int \sigma_{ij}^t \varepsilon_{ij}^t dV / V \quad (7.3)$$

and

$$\Delta E_e^d = -\frac{1}{\rho} \int \sigma_{ij}^d \varepsilon_{ij}^t dV / V. \quad (7.4)$$

It can be analyzed from the above formulations (equations (7.2)-(7.4)), together with transformation temperature interval analysis, the ΔE_e is being relaxed more effectively for the first-half of reverse transformation than its counterpart due to the following possible reasons:

- As shown in Figures 7.2 and 7.3, the value of ε_{ij}^t generated for the first-half of reverse transformation is, by and large, greater than its counterpart (i.e. $\varepsilon_{R1} > \varepsilon_{R2}$). Thus, for a two-step reverse transformation undergone thermal cycling with the external stress σ_{ij} , first-half of reverse transformation produces a larger release of ΔE_e^s .
- The elastic accommodation of transformational shape change involves the buildup of transformation-induced strain energy ΔE_e^t , which opposes the further growth of a martensitic plate [199]. The buildup of ΔE_e^t is therefore partially

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responsible for the prolonged undercooling ΔM in the 1st cooling. Evidently, ΔM increases with increases with increasing magnitudes of σ_{ij} and pre-strain as a function of %RM, as shown in Figure 7.8. The release of ΔE_e^t is directly reflected by the prolonged superheating of the first-half of reverse transformation, ΔA^1 , as shown in Figures 7.9(a) and 7.10(a). It is also evident from Figures 7.9 and 7.10 that the degree of superheating ΔA^1 tends to be larger than its counterpart ΔA^2 regardless of %RM (except for the case of 50MPa, where localized nature of martensite deformation causes merely little difference in them). This indicates larger release of ΔE_e^t for the first-half of reverse transformation.

- The evidence of non-identical slope generated between the 1st cooling ΔM and the first-half of reverse transformation ΔA^1 under 350MPa (Figure 7.5(c)), however, is ascribed to the plastic accommodation of the ΔE_e^d . As discussed earlier in Section 5.1.4, the 350MPa cycling was observed to promote the generation of internal back stress. Following the same thought that the elastic

Figure 7.8 The characteristic of transformation temperature interval ΔM (measured during 1st cooling under constraint) as a function of fraction of retained martensite and thermomechanical treatment conditions: (a) variable constrained stress (50MPa not shown here due to its complex two-step forward transformation); and (b) variable pre-strain with 200MPa cycling.

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energy arising from defects ΔE_e^d can change its sign (positive/negative) depending on the nature of σ_{ij}^d [255], the presence of internal back stress not only to counteracts against the ΔE_e^s and ΔE_e^t but also to annihilate the thermodynamic restoring force responsible for the memorization of kinetic stop imposed at T_H . This explanation could explicitly underline the origin of lack of thermomechanical driving force in the second-half of reverse transformation, discussed by other researchers [69].

- Comparing Figure 7.5(b) and (d), the apparent rise of M_s -temperature for the case of 13% pre-strain indicates the development of dominant internal forward

Figure 7.9 The evolution of first-half and second-half of reverse transformation temperature interval (ΔA^1 , ΔA^2) as a function of fraction of retained martensite and variable constrained stress conditions.

Figure 7.10 The evolution of first-half and second-half of reverse transformation temperature interval (ΔA^1 , ΔA^2) as a function of fraction of retained martensite and variable pre-strain with 200MPa cycling conditions.

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stress, which promotes the dislocations rearrangement to reduce the A_s-T_H . This rearrangement enhances the favorable increase in the ΔE_e^d due to increase in the magnitude of σ_{ij}^d . However, basing on the fact that the σ_{ij}^d developed by constrained thermal cycling is substantially smaller than the constrained stress σ_{ij} in the early number of cycles [53, 57], it would lead one to the conclusion that, on the whole, the first-half of reverse transformation relaxes larger elastic strain energy E_e than its counterpart.

7.2.2 Calorimetric Study of Two-step Transformation

An occurrence of two-step reverse transformation has been observed traditionally by the DSC incomplete endothermic heat flow [66-75]. The heat flow interrupted at a temperature, T_H , between austenite start and finish temperatures (A_s , A_f) produces a kinetic stop, T_K , in the next complete endothermic heat flow. Figure 7.11(a) and (b) respectively shows the endothermic and exothermic heat flow of an as-annealed specimen subjected to low %RM incomplete transformation at 2nd heating. Note that fully transformed endothermic/exothermic curves generated during 2nd heating/cooling are embedded in the figure as a benchmark.

When majority of the self-accommodated martensite reverse transforms into austenite in the 2nd heating, where T_H was imposed at near 80°C after the peak temperature A_p , the immediate lowering of temperature below M_f in the 2nd cooling bring those transformed austenite back to martensite. The exothermic transformation enthalpy reduces to $H_P = 19\text{J/g}$ compared with $H_F = 23\text{J/g}$ of fully transformed condition. In the complete transformation of 3rd heating generates two-step reverse transformation, where the first-step is characterized by the broad endothermic

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Figure 7.11 DSC results showing the evolution of incomplete transformation-induced two-step reverse transformation of an undeformed as-annealed specimen subjected to low %RM condition: (a) endothermic heat flow; and (b) exothermic heat flow.

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peak, followed by the second-step with relatively narrower peak representing reverse transformation of the retained martensite.

Despite the slight temperature difference between T_K and T_H (measured to be 3.1°C , as shown in the inset of Figure 7.11(a)), each of the step transformation almost immediately progresses with increasing temperature. Important to note is that the temperature difference $T_K - T_H$ reduced to 2.6°C when subjected to high %RM condition (i.e. T_H imposed before A_p , as shown in Figure 7.12(a)). This observation is comparable to what was observed earlier in the strain-temperature measurements (cf. Figure 7.7). Besides, from Figure 7.12(a) the pre-positioning phenomenon of the A_s -temperature is more pronounced for the high %RM condition, i.e. the A_s' shifts to about 61°C from the original A_s positioned at about 68°C . In contrast, under low %RM condition, the position of A_s' remains virtually unchanged (Figure 7.11(a)). This observation is also in good agreement with the strain-temperature analysis results (Figure 7.6).

It is apparent that the pre-positioning phenomenon observed under high %RM condition occurs due to the creation of elastic strain energy. In Figure 7.12(b), the shift of M_p to a lower temperature is detectable during 2nd cooling (i.e. decreases from 46 to 43°C) and the inset shows that it is accompanied by the severe modification of the exothermic curve. The elastic energy stored in the course of retransforming martensite relaxes in the next heating, whereby the first-half of reverse transformation gets promoted to a lower temperature range ($A_s \rightarrow A_s'$).

In the low %RM condition, however, there is neither apparent change in M_p nor modification in the exothermic curve due to incomplete transformation (Figure 7.11(b)). Thus, the creation of elastic energy would be insignificant to pre-position the first-half of reverse transformation (i.e. no changes between A_s and A_s').

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Figure 7.12 DSC results showing the evolution of incomplete transformation-induced two-step reverse transformation of an undeformed as-annealed specimen subjected to high %RM condition: (a) endothermic heat flow; and (b) exothermic heat flow.

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At this point, it is important to discuss the change in transformation enthalpy, H , in view of thermodynamic balance equation (6.22). It can be seen that there is only negligible difference in the values of $\Delta H_{net}^{M \rightarrow A}$ measured between 2nd heating and 3rd heating (Figures 7.11(a) and 7.12(a)). Moreover, the $\Delta H_{net}^{M \rightarrow A}$ measured in the two-step reverse transformation is practically the same regardless of the %RM condition. From this observation, a new approach is needed to distinguish the degree of ΔH_{el} produced in association with the pre-positioning mechanism of the first-half of reverse transformation. In this way, the $\Delta H_{net}^{M \rightarrow A}$ generated in the first-half and second-half of the reverse transformation has been isolated (H_1 and H_2). The results are shown in Figure 7.13. Clearly, for the case of low %RM condition, the summation of H_1 and H_2 equals to 21.1J/g which makes the reduction of $\Delta H_{net}^{M \rightarrow A}$ from the 2nd heating to be 1.9J/g. In the same way, the reduction of $\Delta H_{net}^{M \rightarrow A}$ for the high %RM condition is measured to be 2.3J/g. Thus, the difference of $H = 0.4J/g$ has at least contributed toward the pre-positioning of the first-half of reverse transformation.

In essence, the thermomechanical mechanism linked with the degree of overheating $T_K - T_H$ or $A_s - T_H$ (as in the case of strain-temperature analysis) boils down

Figure 7.13 DSC results showing the analysis on the two-step reverse transformation peaks: (a) enlarged view of Figure 7.11(a), low %RM condition; and (b) enlarged view of Figure 7.12(a), high %RM condition.

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to the accommodation process of distinctively oriented martensite variants. In DSC measurement, despite the deformation-free condition, it was apparent that each of the endothermic curves generated in the two-step reverse transformation were characterized by having two distinctive profiles (Figure 7.13). The first-half of reverse transformation, on one hand, showed gradual transforming profile. The second-half of transformation, on the other hand, showed sharp pointed peak and with distorted transforming profile for the high %RM condition.

Linking the DSC observations to the strain-temperature analysis results (Figures 7.6 and 7.7), it is concluded that the degree of overheating decreases with increasing fraction of retained martensite. Such phenomenon occurs due to increased elastic strain energy in the first-half of reverse transformation.

7.3 Two-step Transformation Model

In this section, two-step transformation model will be established for the partially transformed conditions, namely Test (1b), (2b) and (3b). The model will represent the intricate shape recovery behaviors of SATWME and TWME through conceptualization of the internal forward and back stress formations (experimentally observed in Section 5.4), and relating such concept to the dislocation pile-up theory.

Fundamentally, the plastic deformation propagated in single-crystal and polycrystalline materials differs greatly by the fact that, in the latter, the individual crystals have different orientations. The critical shear stress on the slip plane resolved in the slip direction τ_r varies from grain to grain – the orientation dependence is thus averaged out by the Taylor factor M [101]:

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$$\tau_r = \frac{\sigma}{M} \quad (7.5)$$

where σ is the external tensile stress. Experiments have shown [239] that undergoing partial transformation generates density of dislocations. In general, a dislocation will be partly edge and partly screw in nature, taking the form of curves or loops [102]. As has been observed by Hamilton et al. [24], the thermomechanically treated NiTi specimen indeed contains density of dislocation loops. In the case of partial transformation process, it is considered that a retransforming martensite plate forming (in the presence of retained martensite) under an external stress cannot be accommodated elastically, so that some dislocation pile-up occurs at the mismatched boundary. Beside the possible asymmetry of slip that results in a difference in the magnitude of internal forward and back stress (σ_i^F, σ_i^B), it is likely that the preferred slip plane for a particular orientation differ in the grains containing detwinned/reoriented martensite (ORT-*M*) and stress-assisted martensite (PRT-*M*), as illustrated in Figure 7.14. The dislocations piled up at the mismatched boundary of the locally slipped regions have an internal stress field. If the preponderance of σ_i^F over σ_i^B prevails, then the retransformation process of $A \rightarrow$ PRT-*M* during cooling would be assisted by the σ_i^F .

Following the microstructural mechanism and the TWME put forward earlier in Section 5.4, the establishment of dislocation model and two-step transformation model will be discussed in detail in the sub-sections. In Section 7.3.1, the two-step transformation model of 50MPa will be established to account for the effects of back stress formation on the SATWME and TWME. Section 7.3.2 will cover the two-step transformation model of 200 and 350MPa. It is to note that, for the case of 200MPa,

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Figure 7.14 Schematic of a slipped geometry due to martensite pre-deformation and partial transformation, showing the coexistence of ORT- M and PRT- M variants in a localized slip region. The symbol ($\perp$) represents the lattice dislocations, which reside along the trace of the preferred slip planes.

particular attention will be paid to identify the cause of the improvement observed in TWME. On the basis of the two-step transformation model established for the 200MPa, the effects of retained martensite on the SATWME and TWME for the repeated cyclic conditions will be discussed in Section 7.3.3.

7.3.1 50MPa Condition

To begin with, if the NiTi wire specimen is subjected to an externally applied tensile force F , it will deform in such a way that the slip plane (generated as a result of progress in martensite deformation) rotate toward an orientation parallel to the loading axis [264]. This is schematically illustrated in Figure 7.14. Based on such understanding and on the consideration of single-ended pile-up for simplicity, the two-step transformation model of 50MPa has been produced in Figure 7.15 (note that the martensite deformation process and the partial reverse transformation process

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through arrested temperature in the 1st heating are omitted in the figure, since these processes are illustrated earlier in Figure 5.16).

In the 1st cooling, it is assumed that the forward transformation progresses from left to right (Figure 7.15(a-i)). During the course of transformation, nucleation and growth of stress-assisted martensite variants (PRT-*M*) takes place in the presence of retained variants (ORT-*M*). The orientation mismatch between ORT-*M* and PRT-*M* variants is plastically accommodated by forming a mismatched boundary. The dislocations will pile-up against this boundary and the progress of dislocation generation will seize at equilibrium where a shear stress on the preferred slip plane resolved in the slip direction equal to a back stress [265].

Suppose there are cluster of n dislocation loops lying on this slip plane. From the basic dislocations theory [102, 266], it is assumed that these loop configurations to be characterized by a mixture of screw and edge dislocations with diameter L (Figure 7.15(a')). The dislocation as a whole is defined by the total slip line length l and spacing d , which in turn causes the strain increment $d\varepsilon$. If N dislocation sources per unit volume emit n dislocation loops of average diameter L , then the $d\varepsilon$ is defined by [100]

$$d\varepsilon = \frac{\pi L^2 n b}{4} dN \quad (7.6)$$

where b is a Burgers vector. The number of dislocation loops in the pile-up under a resolved shear stress τ_r scaling with the total slip line length l is defined as [101, 102]

$$n = \frac{k \pi \tau_r l}{G b} \quad (7.7)$$

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(a) Constrained thermal cycling (SATWME)

(b) Stress-free thermal cycling (TWME)

Figure 7.15 Schematic of a two-step transformation model (50MPa).

where k equal to 1 for screw dislocations and $1 - \nu$ for edges (ν is a Poisson's ratio),

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and G is the shear modulus. Now recall that the τ_r is defined by equation (7.5). In view of classical plasticity, Mori and Tanaka [103], Mura [104], Sun and Hwang [105, 106] made an attempt to formulate the combined effect of applied external stress, σ_{ij} , and the average volume of internal back stress formation, $\langle \sigma_{ij} \rangle_B$, in the matrix, given by

$$\sigma_{ij}^M = \sigma_{ij} - \langle \sigma_{ij} \rangle_B. \quad (7.8)$$

In general, it is known that the presence of $\langle \sigma_{ij} \rangle_B$ hinders the progress of plastic deformation in the forward direction (tension), and promotes the plastic flow in the reverse direction (compression), and as such, it is manifested by the Bauschinger effect [102, 104].

In the present research, however, the presence of back stress was detected by the decrease of M_s -temperature. Now, by substituting the equation (7.8) into formerly defined thermodynamic criterion of transformation (*see* equation (4.1)), it can be shown that the decrease of M_s occurs as a result of internal back stress formation, i.e.

$$\Delta G_{net}^{A \rightarrow M} = [B(T - M_s)V_M] - \left[\int_V (\sigma_{ij} + \sigma_{ij}^F) \varepsilon_{ij}^M dV + \frac{1}{2} \int_V (\sigma_{ij} - \sigma_{ij}^B) \varepsilon_{ij}^M dV \right]. \quad (7.9)$$

Thus, it can be further interpreted from equation (7.9) that the formation of internal back stress σ_i^B counteracts the effects of applied external stress σ_{ij} and internal forward stress σ_{ij}^F during transformation. In this way, if we incorporate the evolved internal forward/back stresses, the lattice friction stress due to dislocation pile-up [267]

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and the polycrystalline aggregates (i.e. Taylor factor M) into the dislocation model (equation (7.7)), it is further defined as

$$n = \frac{k\pi l \left[(\sigma + \sigma_i^F - \sigma_i^B) / M - \tau_f \right]}{Gb}. \quad (7.10)$$

The expression inside the square bracket represents the effective shear stresses that are induced by the partial reverse transformation. By substituting equation (7.10) into (7.6), the strain increment $d\varepsilon$ due to dislocations pile-up finally reads

$$d\varepsilon = \left\{ \frac{k\pi^2 l L^2 \left[(\sigma + \sigma_i^F - \sigma_i^B) / M - \tau_f \right]}{4G} \right\} dN. \quad (7.11)$$

Thus, it can be predicted that, during 1st cooling, the amount of martensitic strain, ε_{MA} , decreases as a consequence of dislocations pile-up defined by $d\varepsilon$ in equation (7.11). In general, the value $d\varepsilon$ increases with increasing amount of retained martensite (i.e. $ORT-M$), given that the operation of dislocation source N increases. Obviously, here we consider that the $ORT-M$ would act as an obstacle against the nucleation of $PRT-M$. However, based on the observation that ε_{MA} change is relatively small with increasing amount of retained martensite (Figure 5.2(a)), the possibility of dislocation pile-up due to partial reverse transformation under 50MPa cycling would be small.

In the 2nd heating, two-step reverse transformation occurs (Figure 7.15(a-ii)). To overcome the barrier created by the pile-ups, it is necessary to apply extra heating ($A_f' \rightarrow A_s$) to initiate the transformation in the second-half. The application of 50MPa constrained stress causes the persistence of nucleating $PRT-M$ to deteriorate quickly

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after about 5%RM (denoted by the solid down triangle in Figure 7.2(a)). This results in the weakening of internal back stress σ_i^B and the strain relation $\varepsilon_{R1} < \varepsilon_{PT}$ prevails thereafter %RM. Despite the decrease of ε_{R1} , the decrease of SATWME is being suppressed by the possible twofold mechanisms: i) the remnant of self accommodating martensite gets detwinned by the creation of internal stress such that the recovery strain ε_{R2} increases slightly more than ε_{RM} , i.e. $\varepsilon_{R2} > \varepsilon_{RM}$ (Figure 7.2(a)); and ii) the preponderance of internal forward stress σ_i^F over σ_i^B promotes the rearrangement of dislocations and thereby suppresses the further decrease of ε_{R1} relative to ε_{PT} .

The disappearance of two-step transformation in the subsequent stress-free 2nd cooling (Figure 7.15(b-i)) indicates that pile-ups disappear through relaxation processes on removal of constrained stress. Although nucleation of *R*-phase is a very

Figure 7.16 Development of TWME for the specimen undergone 50MPa constrained thermal cycling with various fractions of retained martensite (for ease of comparison, all the strain-temperature curves shown in the figure have been normalized to zero strain at the completion of unloading).

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unlikely scenario for the case of 50MPa (due to the preponderance of σ_i^F over σ_i^B), the presence of σ_i^B after unloading is likely, and as such, it causes the retention of modified dislocation substructures that are unfavorable to TWME. This contention is supported by the fact that the strain-temperature slope of TWME during 2nd cooling modifies more with increasing fraction of retained martensite, as shown in Figure 7.16. In the subsequent 3rd heating (Figure 7.15(b-ii)) the preferentially oriented martensite reverse transforms into austenite, after which completes the development of TWME.

In light of the phenomenological model [44, 268], the relation between the type of internal stress formed and the TWME will be further discussed in the next sub-sections.

7.3.2 200 and 350MPa Conditions

For the case of 200MPa, the characteristic of two-step reverse transformation observed under various pre-strain conditions can be classified into two major categories, i.e. with respect to the dominance of *ORT-M* and *PRT-M* variants. It was apparent from Tables 7.2 and 7.3 that the results obtained from 4 and 8% pre-strain were classified under *PRT-M* dominant category, while the remaining 13, 18 and 23% were classified under *ORT-M* dominant category.

In line with the above classification, the explanations given earlier for the 50MPa condition are similar to those 200MPa cases corresponding to *ORT-M* category. However, distinct from the 50MPa condition is that the effects of retained martensite have shown greater detrimental impact on the SATWME (Figure 5.14), while showing little impact on the TWME (Figure 5.15). In polycrystalline material, it is customary to think that the greater the degree of deformation (200MPa), the more dislocations is produced in the microstructure. The increased density of dislocations

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will reduce the dislocations mobility to move freely during forward and reverse transformations. This makes the accommodation process of *ORT-M* and *PRT-M* difficult in the 1st cooling. For this reason, dislocation pile-up increases with increasing magnitude of pre-strain and the resulting pile-up annihilates the stress-assisted martensite variants formerly retransformed by the constrained cooling. This causes more detrimental effect on the SATWME.

In addition to the explanation given earlier in Section 5.4, the cause of the minimum change in TWME due to partial transformation is further explained in light of Tanaka's phenomenological model [44]. This model was extended by Zhang et al. [268] to include the effects of internal stress field, σ_{INT} , on the development of TWME, represented by

$$\sigma - \sigma_{INT} - \sigma_0 = D(\varepsilon - \varepsilon_0) + \Omega(\xi - \xi_0) + \Theta(T - T_0) \quad (7.12)$$

where D is the Young's modulus, Ω the transformation tensor, Θ the thermoelastic tensor, and $(\sigma_0, \varepsilon_0, \xi_0, T_0)$ represent the initial state/conditions of the stress, strain, martensite ratio, temperature, respectively. In principle, the presence of σ_{INT} assists the thermomechanical cycling of the shape memory alloy (*see* Section 4.4, Chapter 4), whether initiated by thermally-induced shape memory effect cycling or by the stress-induced pseudoelastic cycling. Thus, it is more precise to represent the equation (7.12) as

$$\sigma + (\sigma_i^F - \sigma_i^B) - \sigma_0 = D(\varepsilon - \varepsilon_0) + \Omega(\xi - \xi_0) + \Theta(T - T_0) \quad (7.13)$$

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where the presence of σ_i^F assists the transformation (e.g. as in the case of pseudoelastic cycling, less applied stress is required to initiate the martensitic transformation), while σ_i^B obstructs the course of transformation. Considering the stress free cycling (i.e. $\sigma - \sigma_0 = 0$) and rearranging equation (7.13), we have

$$\varepsilon_{TW} = \frac{(\sigma_i^F - \sigma_i^B) - \Omega(\xi - \xi_0) - \Theta(T - T_0)}{D} \quad (7.14)$$

where ε_{TW} equates to $(\varepsilon - \varepsilon_0)$. It is evident from the equation (7.14) that internal back stress directly lowers the magnitude of TWME.

Figure 7.17 Development of TWME for the specimen undergone 200MPa constrained thermal cycling with various fractions of retained martensite and pre-strain magnitude: (a) 8%; (b) 13%; (c) 18% and (d) 23%.

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For the case of 8% pre-strain, the strain-temperature slope of TWME during 2nd cooling modifies more with increasing fraction of retained martensite, as shown in Figure 7.17. Similar results are seen for the case of 350MPa (Figure 5.4(b)), which is classified under the same PRT-*M* dominant category as the 8% pre-strain, 200MPa. The back stress causes the retention of dislocation debris imparted from partial reverse transformation and with which lowers the TWME. In contrast, for the cases of 13, 18 and 23%, the strain-temperature slope of TWME is virtually unaffected by the partial reverse transformation (Figure 7.17). Based on equation (7.14) and on the observations of strain-temperature curve, it can be concluded that the preponderance of σ_i^F over σ_i^B , as observed in the cases of 13, 18 and 23% pre-strain (ORT-*M* dominant), prevents the specimen from having decreased TWME.

The cause of the increased TWME due to partial reverse transformation is now discussed. For the specimen subjected to 23% pre-strain and with 200MPa constrained stress, sudden drop in M_s -temperature was observed at 71%RM (Figure 5.18). To our surprise, with this decreased M_s the magnitude of TWME improved from the fully transformed condition (Figure 5.15). With reference to the strain-temperature results (Figure 7.17(d)), however, the decrease of M_s is suggested to be not directly connected to the creation of internal back stress, since there is no clear evidence of contractive strain recovery in the stress-free cooling. Thus, two other possible mechanisms are suggested: first mechanism is the operation of certain cross-slip mechanism [100] that is capable of relaxing the plastic deformation. In general, cross-slip mechanism is characterized by [269] “*the conservative motion of a dislocation from one glide plane into another nonparallel plane,*” as schematically illustrated in Figure 7.18.

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In Figure 7.18(a), a number of dislocation loops, which are directed by the Burgers vector b in the first place, glides along the preferred slip plane in the PRT- M region. The shear stress τ causes expansion of the loop. However, as the transformation progresses with high retention of ORT- M variants, the local stress field intensifies due to stress concentration at the mismatched boundary. It is evidenced by the notable increase in M_s with increasing retained martensite (Figure 5.18). Following the works of Washburn [269] and Hull and Backon [101], this intensified local stress field σ_i the so-called interaction stresses generated at the mismatched boundary can redirect the screw part of dislocation loops to expand in the direction of ORT- M slip plane. This causes the part of loops to cross-slip, as illustrated in Figure 7.18(b) and (c). The aftermath of cross-slip is the relaxation of stress concentration at the mismatched boundary, i.e. the closely spaced pile-up of dislocation loops of opposite sign may cancel each other at the boundary, resulting in the decrease of M_s .

In addition to the redirecting mechanism of dislocation motion due to internal stress built-up, when thermally activated cross-slip of screw dislocations starts to take

Figure 7.18 Schematics of cross-slip process occurring at an ORT- M and PRT- M mismatched boundary.

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place, it causes an increase in the mobile dislocation density [270]. The mobile dislocations carry the plastic strain, which travels through the nucleation sites of PRT- M during transformation such that the recovery strain ε_{R1} decreases relative to ε_{PT} . More specifically, the mobile dislocations ρ_m travels through an average slip length $\bar{l}$ toward the direction designated by Burgers vector b . This leads to the generation of plastic shear strain γ formulated as [101]

$$\gamma = \varepsilon M = b \rho_m \bar{l}, \quad (7.15)$$

and rearranging the above equation with respect to strain ε gives

$$\varepsilon = \frac{b \rho_m \bar{l}}{M}. \quad (7.16)$$

Now, the strain increment $d\varepsilon$ imposed by the changes in retained martensite dN can be formulated as

$$\frac{d\varepsilon}{dN} = \frac{b \rho_m}{M} \frac{d\bar{l}}{dN} = \frac{b \rho_m l_{cs}}{M} \quad (7.17)$$

where l_{cs} , defined by the derivative $d\bar{l}/dN$, is the effective distance that mobile dislocations could travel due to cross-slip mechanism. In so doing, the total decrease of recovery strain due to dislocations pile-up and cross-slip now reads

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$$d\varepsilon = \left\{ \frac{k\pi^2 l L^2 [(\sigma + \sigma_i^F - \sigma_i^B)/M - \tau_f]}{4G} \right\} dN + \left(\frac{b\rho_m l_{cs}}{M} \right) dN. \quad (7.18)$$

Thus, the activation of cross-slip mechanism on one hand further decreases the SATWME, but on the other promote the microstructural reconfigurations of ORT-*M* region. When the constrained stress is removed, the pile-ups due to orientation mismatch of ORT-*M* and PRT-*M* disappear, but much of the localized slip will remain. The strain-temperature curve of the TWME (Figure 7.17(d)) suggests that the improvement is effected by rearrangement of the existing randomly oriented dislocations into aligned network. That is, the observation that the inclined slope of the stress-free cooling gets straightened after subjected to 71%RM is the direct indication of the mitigation of microstructural anisotropy [242].

Second mechanism is due to the interaction of ORT-*M* and PRT-*M*. It has been suggested that competition of these distinctively oriented martensite variants impinging onto each other forms preferential dislocations [271]. It is further suggested that the creation of new sites and embryos by this plastic deformation could lead to a strain-induced nucleation of martensitic transformation [262, 272]. This leads to the improvement of TWME.

7.3.3 Repeated Cycling under 200MPa Conditions

Based on the two-step transformation model produced in Figure 7.15, and on the dislocation and phenomenological theory formulated in equations (7.11) and (7.14), attempts were made to further understand the effects of internal stress formed on the SATWME and TWME. Recall from Figure 5.19 that the four different cyclic conditions were considered: i) full transformation; ii) partial transformation at 1st

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heating; iii) partial transformation at 1st and 3rd heating; and iv) partial transformation at 4th heating. The discussion for the case of ii) is similar to the one put forward earlier in Section 7.3.2 and is omitted here. Particular attention, however, is paid to the case when dislocation pile-up occurs due to mismatch of retransforming stress-assisted martensite (SAM) and retained SAM variants.

As an extension of discussion put forward earlier in Section 5.6, the development of internal stress is studied through DSC measurement of the post-trained specimens and the results are shown in Figure 7.19. The reverse transformation temperatures and enthalpy measured directly from the DSC curves are summarized in Table 7.4. It is evident from Table 7.4 that the martensite stabilization effect had occurred for the cases of cyclic condition i) and ii) where their A_s temperatures in the 1st heating increased from the as-annealed (68°C, *see* Figure A.3). In contrast, the remaining two cyclic conditions iii) and iv) did not show any sign of stabilization effect. A previous study [86] suggested that in a polycrystalline matrix, deformation by martensite reorientation creates an internal stress field in the same direction as the oriented martensite. This internal stress creates resistance to the reverse transformation, thus the A_s -temperature increases. In this respect, for the case of cyclic conditions i) and ii), it is consistent to witness the rise of A_s in their first heating of DSC since the repeated

Figure 7.19 Effect of various cyclic conditions imposed during training on the DSC curves: (a) endothermic heat flow; and (b) exothermic heat flow.

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Cyclic condition	First heating			Second heating			
	A_s (°C)	A_f (°C)	ΔA (°C)	A_s (°C)	A_f (°C)	ΔA (°C)	ΔH (J/g)
i) Full transformation	76	91	15	57	72	15	14
ii) Partial trans. at 1 st heating	74	90	16	59	72	13	15
iii) Partial trans. at 1 st and 3 rd heating	67	83	16	60	71	11	16
iv) Partial trans. at 4 th heating	67	84	17	59	71	12	16

$$\Delta A = A_f - A_s.$$

Table 7.4 The transformation temperatures and enthalpy of post-trained specimens measured from DSC curves shown in Figure 7.19.

full transformation enabled progressive increase of M_s -temperature during training to produce an oriented internal stress. In other words, despite the presence of R -phase in the DSC result (Figure 7.19(b)), which effectively indicated the formation of internal back stress, much of the internal forward stress dominates over the back stress to promote the TWME (cf. equation (7.14)).

For the case of cyclic condition iv), the rise of M_s at 4th cycle (Figure 5.19(d)) also indicated the development of internal forward stress, which is comparable to the under stressing phenomenon of the partially transformed stress-induced cycle [273]. However, clear contrast is seen in the decrease of A_s -temperature in the first heating of DSC. Based on this result, it should be emphasized again that dislocation pile-ups due to partial reverse transformation bring about the formation of both internal forward and back stress, and much of the pile-ups are retained by the back stress. Clearly, it was shown earlier that the retention of the pile-ups debris was reflected by the $\Delta\epsilon_{IR}$ (see Section 5.5.1, Chapter 5). Thus, internal stress developed by the repeated full transformation cycling is favorable to the TWME, because of the dominant internal forward stress formation against the back stress.

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Another feature to highlight from Figure 5.19(a)-(d) is that the magnitude of SATWME was less affected by the retained martensite when the partial reverse transformation was imposed at the higher number of training cycle. Compared with the full transformation condition, for the case of cyclic condition i) partial transformation at 1st heating, the value of ε_{SATW} decreases by $[(4.87-3.77)/4.87] \times 100\% = 23\%$. In contrast, for the case of cyclic condition iv) partial transformation at 4th heating, the value of only decreases by $[(5.95-5.62)/5.95] \times 100\% = 5.5\%$. This phenomenon can be explained by the dislocation model (equation (7.11)), and in association with the two-step transformation model produced in Figure 7.20.

From equation (7.11), the focus is on the total slip line length l and Taylor factor M . With reference to works by Seeger et al. [274], it is expected that the progress in total strain deformation (i.e. increase in ε_{MA}) results in the decrease of l . The value of M , on the other hand, is found to be dependent on the deformation modes [275], extent of deformation leading to work-hardening [276, 277] and texture [267]. Thus, following the partial transformation at 1st heating, the subsequent 1st cooling (Figure 7.20(a-i)) produces dislocation pile-up with a relatively large l . Knowing that the deformation progresses further with increased number of cycling, the value of l reduces comparatively if the partial transformation was imposed at later cycle (Figure 7.20(b-i)). In addition to reduced l , it is expected that the value of M increases with increased number of cycling [278, 279]. This implies that, based on equation (7.11), the strain increment $d\varepsilon$ due to dislocation pile-up will be minimized for the cyclic condition iv) partial transformation at 4th heating, in agreement with the experimental observation.

Finally because of the small $d\varepsilon$, it is also consistent to observe that there will be less extra heating required to initiate the second-half of the two-step reverse

7.3 Two-step Transformation Model

(a) Partial transformation at 1st heating

(b) Partial transformation at 4th heating

Figure 7.20 Schematic of a two-step transformation model (repeated cycling under 200MPa).

transformation ($A_f' \rightarrow A_s$, typically 23°C compared to 36°C for the cyclic condition i))

and that the SATWME developed in the 5th heating is virtually unaffected.

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7.4 Further Remarks and Summary

The mechanism of two-step transformation was studied on the basis of experimental and macromechanical approaches in this chapter.

A strain comparison approach demonstrated that the two-step reverse transformation is proceeded by the sequential transformation of retransforming stress-assisted martensite (i.e. PRT-*M*) and retained martensite (i.e. ORT-*M*). The dominance of ORT-*M* and PRT-*M* with respect to varying amount of %RM was demonstrated by the shift of equal strain position. Undergoing 350MPa cycling in particular was dominated by the PRT-*M*, even at high %RM.

The strain-temperature analysis demonstrated that the degree of overheating in the two-step reverse transformation decreases with increasing fraction of retained martensite. The decrease of overheating was accompanied by the enhanced pre-positioning of the first-half of reverse transformation. Based on the elastic strain energy formulations and temperature interval analysis, it is suggested to be driven by the larger release of elastic strain energy.

The pre-positioning and overheating phenomena of two-step reverse transformation were cross-examined by DSC. It was shown that pre-positioning of the first-half of reverse transformation occurred due to modification of the retransforming martensite structures: the broadening of exothermic curve and the shift of M_p to a lower temperature indicated the creation of elastic strain energy. Similar to the strain-temperature analysis, the promoted pre-positioning of the first-half of reverse transformation was accompanied by the decrease of overheating.

The DSC results also indicated that the accommodation process of distinctively oriented martensite variants was reflected by the generation of two dissimilar endothermic curves. The endothermic curve of the second-half of reverse

7.4 Further Remarks and Summary

transformation (retained $M \rightarrow A$) becomes more distorted when large fraction of martensites were retained. This indicates that undergoing partial transformation can impose structural modification to the retained martensite. Appearance of two-step reverse transformation was only temporal in nature. It reverted to single-step endothermic curve in the next full reverse transformation.

The two-step transformation model, in association with the dislocation pile-up theory and phenomenological model, clearly conceptualized the effects of retained martensite on the development of SATWME and TWME under various thermomechanical conditions.

It has been observed thus far in the present experimental and macromechanical studies that the underlying mechanism of TWME for polycrystalline materials lies in the progress of martensite deformation, the accommodation process of orientation-mismatched martensite variants and the dislocations arrangement influenced by the presence of internal stress gradients. From the equal strain position analysis, it is demonstrated that internal back stress formation is promoted by the dominance of PRT- M variants. It makes the accommodation process of ORT- M and PRT- M difficult, due to which immobilizes the dislocations movement in the forward transformation direction, retains the dislocation pile-up debris and causes direct detrimental effect on the TWME.

CHAPTER 8

Conclusions

8.1 Summary

In this thesis, several important contributions have been made in the aspects of two-way shape recovery characteristics in NiTi alloy via experimental and macromechanical approaches.

A series of strain-temperature experiments on near equiatomic polycrystalline NiTi alloy wire subjected to various training conditions were investigated. The aims of this investigation were mainly twofold. First, it was aimed at identifying the predominant factors responsible for the stress-assisted two-way memory effect (SATWME) and the subsequent spontaneous recovery of two-way memory effect (TWME). The second was to characterize the thermomechanical correlation of these memory effects to a martensite deformation. The major conclusions are summarized as follows.

8.1.1 Two-way Shape Recovery Characteristics (Full Transformation)

In the fixed pre-strain with variable constrained stress tests, it was found that the magnitude of stress-assisted two-way memory strain increased to its maximum at

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200MPa. Further increase in constrained stress resulted in the sharp decline of SATWME. Despite the fixed pre-strain at 8%, the martensitic strain measured at the end of constrained cooling indicated the further progression of martensite deformation. A progress in martensite deformation due to repeated constrained cycling resulted in the increase of SATWME and decrease of irrecoverable strain.

The fixed constrained stress tests demonstrated that the shape recovery behavior of SATWME is influenced by the magnitudes of pre-strain or martensitic strain, whichever is greater. The repeated cycling tests further demonstrated that the full utilization of martensite reorientation capacity can be achieved independently of deformation procedures: by the direct application of pre-strain or cyclic shift of martensitic strain to reach near 13% under 200MPa cycling. This training condition resulted in the maximum SATWME.

A modified Clausius-Clapeyron macromechanical model was used to estimate the internal stress developed during training. It was found that at 13% martensitic strain, a maximum accumulative internal stress can only be achieved under 200MPa cycling. The internal stress developed via direct application of 13% pre-strain and single training cycle was found to be significantly smaller than those achieved through martensitic strains. Based on such discrepancy in the development of internal stress, it is concluded that the generation of maximum SATWME is not attributed necessarily to the development of maximum internal stress.

The SATWME and TWME showed a strong correlation of their recovery strain magnitudes as a function of martensite deformation. For a thinner wire, the increase of martensitic strain through constrained cooling determined the increase of SATWME and TWME to their maximum achieved at near 20% strain. The shape recovery behavior of SATWME under 50MPa agreed well with that of TWME. The

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internal stress developed in achieving maximum SATWME and TWME coincided closely at the optimum deformation level. Further coincidence was highlighted by the transformation enthalpy and temperature hysteresis width.

Taking into account the calorimetry observations, it is concluded that the thermomechanical mechanisms involved in the development of SATWME and TWME are highly identical at their maximum, but does not project the same mechanisms below and above the maximum level.

8.1.2 Two-way Shape Recovery Characteristics (Partial Transformation)

In the partially transformed condition, the correlation between SATWME and TWME determined for fixed pre-strain with 50, 200 and 350MPa constrained stress is comparable to that observed in fully transformed condition. The martensitic strain is found to decrease with increasing fraction of retained martensite, which directly affected on the magnitudes of SATWME and TWME.

With variable pre-strain magnitudes, the decrease of martensitic strain due to increase in fraction of retained martensite under 200MPa caused variation in TWME from continuous decrease to a combination of decrease and increase in two-way memory strain. The variation occurs due to whether the martensitic strain exceeded the initial pre-strain magnitude to achieve the optimum martensite deformation for a TWME. The effect of partial transformation on TWME is negligible when the martensitic strain decreases below the initial pre-strain with increasing fraction of retained martensite.

The underlying mechanism of TWME is associated with the internal forward and back stress formations. Partial reverse transformation through thermal arrest during

heating leads to the accommodation of stress-assisted and detwinned martensite variants. Such accommodation process causes the internal forward and back stress formations. On the basis of M_s -temperature increase under 200MPa with increasing fraction of retained martensite, a dominant internal forward stress contributes to the increase in TWME. In contrast, the formation of dominant internal back stress, as reflected by a continuous decrease of M_s under 350MPa, shows hindrance to the progress of forward transformation to lower the martensitic strain, and thus causes the decrease of TWME.

The mechanism of two-step transformation was elucidated by the macromechanical and thermodynamical approaches. A strain comparison approach demonstrated that the generation of two-step reverse transformation is proceeded by the sequential transformation of stress-assisted and detwinned martensite variants in the order of increasing temperature. Undergoing 350MPa cycling in particular was dominated by the stress-assisted martensite, even when large fractions of detwinned martensite were retained. Consequently, from an equal strain position analysis, it is demonstrated that internal back stress formation is promoted by this effect.

The strain-temperature analysis demonstrated that the degree of overheating in the two-step reverse transformation decreases with increasing fraction of retained martensite. The decrease of overheating was accompanied by the pronounced pre-positioning of the first-half of reverse transformation. Using the data from strain-temperature measurements and those data evaluated with elastic strain energy formulations and temperature interval analysis, the first-half of reverse transformation was found to relax larger elastic strain energy than its counterpart.

In the calorimetry analysis of as-annealed specimen, the pronounced pre-positioning of the first-half of reverse transformation was accompanied by the

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decrease of overheating, as comparable to the strain-temperature analysis results. The calorimetry results also indicate that the appearance of two-step reverse transformation is a one-time only phenomenon and it disappeared in the next full reverse transformation.

A two-step transformation modeling approach incorporated the dislocation pile-up and accommodation process of the distinctively oriented stress-assisted and detwinned martensite variants, the resulting formation of internal forward and back stresses, and the possible cross-slip mechanism. The formation of internal back stress due to partial reverse transformation is shown to be responsible for the retention of dislocation pile-up debris, which acts as a barrier in the subsequent transformation, and as such, it directly influences on the SATWME and TWME.

8.1.3 Factors Responsible for the SATWME and TWME

It is concluded on the basis of thorough experimental and macromechanical analysis pursued in this research that there are four predominant factors responsible for controlling the development of SATWME and TWME:

i) Pre-strain

Determines the utilization of martensite detwinning capacity and the evolution of dislocations;

ii) Constrained stress

Determines the microstructural potency to align/realign the orientation of martensite variants and dislocations during thermal cycling;

iii) Propagation of martensite deformation during thermal cycling

Determines the further reorientation process of martensite variants and the introduction of additional dislocations; and

iv) Nature of thermal cycling (full/partial transformation)

Determines the accommodation process of distinctively oriented stress-assisted and detwinned martensite variants, and the dominance of internal forward and back stress formations.

8.2 Future Work

One door closes and another door opens for future research. This section will highlight some future research directions one could head-on in the areas of experimental and theoretical work.

In the current research focus was given, by and large, on the roles of internal stress in the development of SATWME and TWME. Although careful macromechanical approach had been taken to estimate the degree of internal stress developed during training, further work may be carried out on other experimental and theoretical means to cross-examine the validity of internal stress estimates. Other technique includes but not limited to observing the shift of critical stress in inducing martensitic transformation in the repeated pseudoelastic cycling [186], stress relaxation interpreted through a power relation between dislocation velocity and the effective stress [280], in situ X-ray diffraction [281] and electron backscatter diffraction [234].

The evolution of two-step reverse transformation was captured macroscopically via strain-temperature and DSC observations in this research. In situ microscopic experiments are desired to confirm the following:

- Sequential reverse transformation of distinctively oriented martensite variants;
- One-time only phenomenon of two-step reverse transformation;
- Formation of *R*-phase and its enhancement due to increase in %RM; and

CHAPTER 8. Conclusions

- Dislocation mechanisms responsible for the improvement in TWME.

Another important microscopic aspect deemed worthy of further investigation would be the quantitative measurement of dislocations, e.g. density of dislocations, number of dislocation loops, dislocation loop average diameter, total slip line length and Burgers vector. This could lead to a numerical simulation of the strain increment due to partial reverse transformation using the proposed two-step transformation model. Comparison between the simulated results and the ones with experimental could further lead to a justification of the proposed model, and its accuracy may be improved upon careful estimate of Taylor factor.

In view of Tanaka's phenomenological model [78], *stress-dependent parameter* needs to be incorporated into the material parameter that represents the amount of shift in M_s and A_s temperatures with respect to the volume fraction of retained martensite. The *stress-dependent parameter* should include both externally applied and internally evolved stresses. Further research needs to be done to cross-examine if the aforementioned stress-dependent approach could fit likewise into Brinson Model [152, 282] and/or Liang and Rogers Model [153, 268].

Establishing an accurate model of two-step reverse transformation opens up other possible avenue of exploring high temperature shape memory effect. Experimental results have demonstrated that the transformation temperature window of the two-step reverse transformation can be enlarged significantly. If the specimen imparted with permanent enlarged temperature window, it would be possible to replace the conventional way of adding third element into the binary NiTi alloy [283, 284].

To date, majority of the experimental works on incomplete transformation-induced two-step or multiple-step transformation have been conducted in NiTi alloy [62, 67-72, 74-76, 285-287], NiTi-based alloy [73, 77, 288, 289] and CuZnAl alloy

8.2 Future Work

[66, 67]. Further work may be carried out on other alloy systems to better one's knowledge on the mechanism of two-step transformation. An additional area to explore would be in the improvement and degradation of the TWME after subjected to partial reverse transformation. With increased number of interruption, the reverse transformation temperature window increases and may have a more detrimental effect on the SATWME, but may produce a larger beneficial effect on the TWME.

APPENDIX A

DSC Results of As-annealed Specimen

Figure A.1 DSC thermogram of as-annealed NiTi wire with diameter = 0.508mm specimen (argon gas furnace).

APPENDIX A. DSC Results of As-annealed Specimen

Figure A.2 DSC thermogram of as-annealed NiTi wire with diameter = 0.508mm specimen (open-air furnace).

Figure A.3 DSC thermogram of as-annealed NiTi wire with diameter = 0.185mm specimen (open-air furnace).

APPENDIX B

50N, 500N Load Cell Accuracy

Figure B.1 A copy of load cell accuracy test conducted for 50N load cell.

APPENDIX B. 50N, 500N Load Cell Accuracy

Figure B.2 A copy of load cell accuracy test conducted for 500N load cell.

APPENDIX C

Thermal Expansion of the Grips

In the course of constrained thermal cycling, NiTi wire inevitably experiences compressed hot and cold air blown inside the thermal chamber (cf. Figure 3.5). This directly causes not only the wire but also the pneumatically actuated/mechanical grips to expand or contract according to the temperature variation.

To begin with, the coefficient of thermal expansion (CTE) of the grips were measured by firmly placing the thick glass plate with a dimension approximately $80 \times 30 \times 5.5\text{mm}$ (length $\times$ width $\times$ thickness) between the two grips. Figure C.1 illustrates the setup and configuration of CTE measurement carried out for the 50N load cell arrangement (similar setup was made for the one with 500N load cell, except that upper/lower grips were replaced by the pneumatic grips).

To test the rigidity of the glass plate, a maximum load of 80N (i.e. equivalent to about 400MPa applied to the NiTi 0.508mm diameter wire during constrained cycling) was applied to the 500N load cell arrangement. The load-displacement result is shown in Figure C.2. It can be seen that the displacement merely changed upon reaching maximum load of 80N (about 0.037mm, as denoted by the dashed line). Thus, the glass plate is considered to be rigid during the thermal cycling and would not contribute to the overall displacement. The initial gauge length of the glass plate was held at 60mm. Displacement changes during thermal cycling were recorded under

APPENDIX C. Thermal Expansion of the Grips

CTE of components:

Quartz rod = $0.54 \times 10^{-6}/^{\circ}\text{C}$

Glass plate = $5 \times 10^{-6}/^{\circ}\text{C}$

STAVAX stainless steel (Jaws) = $11 \times 10^{-6}/^{\circ}\text{C}$

Figure C.1 Schematic of CTE measurement setup and configuration (50N load cell arrangement).

Figure C.2 Load-displacement curve of conventional rigid glass plate subjected to a maximum load of 80N.

APPENDIX C. Thermal Expansion of the Grips

Figure C.3 The amount of thermal expansion due to 50N and 500N load cell fixture arrangements.

force-controlled mode. Thermal expansion of the glass plate ($\text{CTE} = 5\text{E-}6/^{\circ}\text{C}$) was removed from the recorded data.

Figure C.3 shows the measurement of CTE conducted for the 50N and 500N load cell fixture arrangement. Evidently, the amount of expansion generated for the 50N load cell is substantially smaller (about $0.57 \times 10^{-3} \text{ mm/}^{\circ}\text{C}$) compared to 500N load cell (about $1.08 \times 10^{-3} \text{ mm/}^{\circ}\text{C}$). By using the conventional linear thermal expansion formula [290], CTE for the 50N and 500N load cells are given by $18 \times 10^{-6}/^{\circ}\text{C}$ and $56 \times 10^{-6}/^{\circ}\text{C}$, respectively. The displacement data points recorded during thermal cycling were corrected according to these CTE values.

APPENDIX D

Reliability of Experimental Results

To guarantee the reliability and reproducibility of experimental results, several thermomechanical tests were performed for the as-annealed NiTi wire with diameter 0.508 and 0.185mm. Figure D.1(a) shows the stress-strain response of as-annealed specimens. Each of the undeformed specimens was subjected to 8% pre-strain. Subsequent to pre-straining is the generation of strain-temperature curve upon 1st heating and cooling under 50MPa, as shown in Figure D.1(b). It can be seen that, among the three trials conducted, there is no significant deviation for the stress-strain and strain-temperature curves.

Figure D.1 As-annealed NiTi wire with diameter 0.508mm subjected to 8% pre-strain and 50MPa constrained thermal cycling: (a) stress-strain curve generated after loading and unloading; and (b) strain-temperature curve generated after 1st heating and cooling under constraint.

APPENDIX D. Reliability of Experimental Results

Figure D.2 As-annealed NiTi wire with diameter 0.185mm subjected to various thermomechanical conditions: (a) 8% pre-strain, 200MPa constrained cycling and partial reverse transformation (15%RM); and (b) 18% pre-strain, 200MPa constrained cycling and partial reverse transformation (21%RM).

In addition to full transformation condition, the strain-temperature curves generated upon partial transformation and various thermomechanical conditions showed an identical path for the 1st and 2nd trials, as shown in Figure D.2. Based on the results (Figures D.1 and D.2), it can be justifiable to say that not only the annealing condition applied to each of the specimens were consistent but also those experimental results obtained in this research are not a mere coincidence.

APPENDIX E

Revised Estimation of Internal Stress

Due to progress in strain deformation during constrained thermal cycling, the revised estimation of internal stress has been made for the Test (2a) condition. Table E.1, E.2 and E.3 summarizes the characteristic of M_s -temperature, characteristic gradient ($\Delta\sigma_{EXT}/\Delta M_s$) extrapolated for the 2nd training cycle and corrected values of internal stress for 50, 200 and 400MPa, respectively. Note that the values of M_s generated at 18% deformation under 400MPa cycling were estimated by the graph shown in Figure E.1.

Figure E.2 shows the relation between M_s and the magnitude of constrained stress. The strict linear relationship found especially for the 18% deformation confirms the reliability of the internal stress estimates.

Total strain deformation (%)	M_s (1 st cooling) (°C)	M_s (2 nd cooling) (°C)	M_s (°C)	$\Delta\sigma_{EXT}/\Delta M_s$ (MPa/°C)	Revised internal stress (MPa)
10	48.32	49.84	1.52	9.24	14.1
13	48.95	50.13	1.18	15.64	18.5
18	47.30	47.55	0.25	10.07	2.52

$$M_s = M_s (2^{\text{nd}} \text{ cooling}) - M_s (1^{\text{st}} \text{ cooling})$$

Table E.1 Collected data for the revised estimation of internal stress (50MPa constrained stress).

APPENDIX E. Revised Estimation of Internal Stress

Total strain deformation (%)	M_s (1 st cooling) (°C)	M_s (2 nd cooling) (°C)	M_s (°C)	Revised internal stress (MPa)
10.1*	62.64	66.07	3.43	31.7
13.0	58.49	59.72	1.23	19.2
18.0	60.00	62.56	2.35	23.7

$$M_s = M_s (2^{\text{nd}} \text{ cooling}) - M_s (1^{\text{st}} \text{ cooling})$$

*Due to lack of experimental data, the level of deformation has been taken as 10%.

Table E.2 Collected data for the revised estimation of internal stress (200MPa constrained stress).

Total strain deformation (%)	M_s (1 st cooling) (°C)	M_s (2 nd cooling) (°C)	M_s (°C)	Revised internal stress (MPa)
16.6	80.49	80.52	0.03	N/A
17.1	81.32	81.76	0.44	N/A
18.6	78.48	82.67	4.19	N/A
22.6	77.23	82.39	5.16	N/A
18.0	79.60*	82.30*	2.70	27.2

$$M_s = M_s (2^{\text{nd}} \text{ cooling}) - M_s (1^{\text{st}} \text{ cooling})$$

*Estimated from Figure E.1.

Table E.3 Collected data for the revised estimation of internal stress (400MPa constrained stress).

Figure E.1 Estimation of M_s -temperature at 18% deformation (400MPa constrained stress).

APPENDIX E. Revised Estimation of Internal Stress

Figure E.2 Evolution of M_s -temperature in relation to the magnitude of constrained stress and total strain deformation.

APPENDIX F

Evaluation of Total Strain Deformation

Figure F.1 highlights some of the strain-temperature curves generated under 50, 200 and 400MPa constrained cycling.

Table F.1 summarizes the degree of total strain deformation progressed due to pre-straining and/or thermal cycling under Test (2a) condition. Note that the values of ε_{MA} are measured at the end of 2nd cooling. The evaluated values of total strain deformation are reflected in the DSC results (Figure 6.3).

Pre-strain (%)	50MPa		200MPa		400MPa	
	ε_{MA} (%)	Total strain deformation (%)	ε_{MA} (%)	Total strain deformation (%)	ε_{MA} (%)	Total strain deformation (%)
3	<i>4.0</i>	4.0	<i>11.3</i>	11.3	<i>21.6</i>	21.6
4	<i>4.8</i>	4.8	<i>10.7</i>	10.7	<i>21.3</i>	21.3
8	7.1	8.0	<i>11.9</i>	11.9	<i>21.4</i>	21.4
10	8.2	10.0	<i>11.7</i>	11.7	<i>21.9</i>	21.9
13	9.8	13.0	11.9	13.0	<i>22.3</i>	22.3
18	13.4	18.0	18.6	18.0	<i>25.4</i>	25.4

Table F.1 Degree of total strain deformation defined for the DSC analysis (Figure 6.3); the values highlighted in italic indicate ε_{MA} being dominant over pre-strain.

APPENDIX F. Evaluation of Martensite Deformation

Figure F.1 The evaluation of strain-temperature curves for the Test (2a) condition.

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