Temperature memory effect/triple-shape memory effect in niti shape memory alloys and shape memory effect in keratin

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TME/TRIPLE-SME IN NITI SMA AND SME IN KERATIN

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**TEMPERATURE MEMORY EFFECT/TRIPLE-SHAPE
MEMORY EFFECT IN NITI SHAPE MEMORY ALLOYS
AND SHAPE MEMORY EFFECT IN KERATIN**

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SCHOOL OF MECHANICAL & AEROSPACE ENGINEERING

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Abstract

Besides the shape memory effect (SME), in which the permanent shape can be recovered at the presence of the right stimulus, the temperature memory effect (TME) is another feature of shape memory materials. The TME refers to a phenomenon that a particular temperature can be memorized in a certain manner. A systematical investigation of the mechanism from energy point of view for the TME in NiTi shape memory alloys (SMAs) is presented based on the results of a series of differential scanning calorimeter (DSC) tests. The traditional approach for the TME is expanded, and a modified one is identified, which can be utilized to monitor over-heating temperature with high accuracy.

The triple-shape memory effect (triple-SME), which is easily achievable in shape memory polymers (SMPs) but not in SMAs, is achieved in a few types of NiTi SMAs. Two approaches, namely small strain program and larger strain program are proposed. The conditions on both material and programming parameters, as well as the mechanisms for the triple-SME, are identified and the influence of programming parameters is investigated.

Both heating-induced and water-induced SMEs in human nail and silkworm silk, in which keratin is their main component, are systematically investigated. The influence of water content is studied. The triple-SME utilizing multiple-stimuli is realized in nail. The fundamentals behind the difference in heating and water based SMEs are studied.

Keywords: temperature memory effect; shape memory alloys; NiTi; triple-shape memory effect; nail; silkworm silk; keratin.

Chapter 1 Introduction

1.1 Background

Smart materials start to play a more and more important role in our current life. So far, many materials are found to be able to change their physical and/or chemical properties when a particular stimulus is applied. These materials are known as the stimulus-responsive materials (SRMs) [1, 2].

Among them, some are able to change their shape in response to the presence of the right stimulus [2, 3]. According to whether the material is able to maintain the deformed “temporary” shape, this sort of materials can be further classified into two types, namely shape change material (SCM) and shape memory material (SMM). Shape change material instantly or gradually changes shape when the stimulus triggering deformation is removed. This is a feature known as the shape change effect (SCE). Piezoelectric materials, such as lead zirconate titanate (PZT), are typical shape change material [4]. Similarly, the elastic deformation of a material is actually a kind of mechano-responsive shape change effect. On the other hand, shape memory material is able to keep the deformed shape unless the right stimulus is applied. Such a feature is termed as the shape memory effect (SME). In other words, after being severely and quasi-plastically distorted, shape memory materials recover their original shapes only when the right stimulus is applied [5, 6]. Typical stimulus for the SME includes heat, stress/pressure, electricity, magnetic field, chemical and light, etc [2, 7-11].

From energy point of view, the essential difference between the shape change effect and shape memory effect is a result of the difference in the energy barrier level [12]. As illustrated in Figure 1.1, upon applying or removal of an external stimulus, the shape of a material may switch between shapes A and B. If the energy barrier is high (H as shown in Figure 1.1), upon removal of the applied stimulus, the material keeps the current state. A right stimulus is required to overcome the high energy barrier for shape switching, so this is the shape memory effect. If the energy barrier is about none, shape change is instant when the applied stimulus is removed. This is the shape change effect. For viscous-elastic materials, in which the shape recovery is gradual, energy barrier is low (H' as shown in Figure 1.1).

Figure 1.1 Illustration of energy barrier between two shapes (A and B). H and H' represent different levels of energy barrier [12].

Figure 1.2 presents various types of shape memory materials and their locations within the world of materials. Among them, shape memory alloy (SMA) and shape memory polymer (SMP) are two major types, which have been extensively investigated. Other types of shape memory materials include shape memory hybrid (SMH) [6, 13, 14], shape memory ceramic (SMC) [15, 16], and shape memory gel (SMG) [17-19], etc. The shape memory composite (SMc) is defined as a composite with at least one shape memory component, usually SMA or SMP [16, 20]. As such,

shape memory composite is not an independent subgroup under shape memory materials.

Figure 1.2 Location of various types of shape memory materials within the world of materials [1].

The investigation of SMAs started from AuCd and AgCd in 1930s, followed by probably the most significant discovery in NiTi, and a number of other alloy systems [21]. So far, NiTi with/without a tertiary metal element alloy system is the most intensively studied SMA. It has excellent biocompatibility and resistance to corrosion [22, 23], and most importantly, shows strong SME and/or super-elastic behavior, which is the ability to recover instantly when the applied stress is removed at high

temperatures (which is essentially the feature of the shape change effect). As such, NiTi-based SMAs are ideal for actuators, particularly in biomedical applications. On the other hand, Cu-based SMAs, for instance, CuAlZn and CuAlNi, are attractive alternative to NiTi due to their relatively lower cost and better electrical and thermal conductivity, etc [24-27]. Some other types of SMAs, e.g., Fe-based alloys, have also been developed, but are much less popular due to some disadvantages of their own, in particular, poor SME [5].

The underlying mechanism behind the thermally induced SME in SMAs is the reversible martensitic transformation between high temperature austenite and low temperature martensite. A typical SME cycle of SMAs is illustrated in Figure 1.3. Starting from point *B*, martensite (twinned) is stretched and experiences a process called “detwinning”. After unloading (from point *C* to point *D*), residual deformation is resulted. When being heated, martensite (detwinned) transforms into austenite through path $\overline{DEFA}$ to recover its original shape. Upon cooling from point *A* to point *B*, austenite transforms to twinned martensite without involving any macroscopic shape change.

Figure 1.3 Stress-strain-temperature relationship of thermo-responsive SMA in a typical SME cycle [21].

Besides thermo-responsive SMAs that are activated by heating, there are magneto-responsive SMAs as well. This type of SMAs, for instance Ni-Mn-Ga alloys, can be triggered by applying a static or alternating magnetic field [28, 29]. The underlying driving mechanism is also reversible martensitic transformation although the required stimulus is different.

SMP was first “officially” introduced in 1984 [20]. Since then, various types of SMPs have been invented, such as polyurethanes [30-33], poly(styrene-block-butadiene) [34-36] and polynorbornene [37, 38], etc. As compared with SMAs, SMPs normally have a far larger recoverable strain, lower density and low cost (both in terms of material and processing) [39]. Moreover, the properties of SMPs can be easily tailored by means of adding fillers or varying compositions [40-43]. Apart from direct heating, SMPs can also be triggered by light [44, 45], electricity [46, 47], moisture [48-50], solvent [51], magnetic field [52, 53], etc.

Figure 1.4 shows a typical SME cycle of a thermo-responsive SMP. At high temperatures a SMP becomes soft and can be easily stretched (1). After maintaining

the deformed shape for a while (2), and then cooling, the free standing SMP is able to largely keep the deformed shape (3). This process is to deform a piece of SMP into a temporary shape and is called “programming”. Re-heating results in the SMP restoring its original shape (4).

Figure 1.4 Typical thermo-mechanical cycle of the SME in a SMP [54].

1.2 Objectives

In addition to the SME, the temperature memory effect (TME) and the triple-shape memory effect (triple-SME) have been identified as two other common features of shape memory materials. TME is a phenomenon when a shape memory material experiences an interruption during heating process, and this interruption temperature can be memorized during the next complete heating. Although the TME was firstly reported in SMAs, the actual mechanism for that in SMAs has yet been confirmed with solid evidence, and no potential applications of the TME in SMAs has been spotted.

On the other hand, triple-SME refers to the shape recovery from a temporary shape to the permanent shape through one intermediate shape, i.e., totally three shapes are

involved. Triple-SME has already been realized in SMPs, but we have yet found a way to realize the triple-SME in SMAs in a manner as that in SMPs.

So that, the first objective of this dissertation is to investigate the fundamentals behind the TME in SMAs and the possibility to realize the triple-SME in them, together with the potential applications of both effects.

Till today, the investigation of various shape memory phenomena in polymeric materials is largely limited to traditional polymers, including conventional engineering polymers. Non-conventional polymeric materials, such as natural bio-polymers and protein, are seemingly out of the scope.

Hence the second objective of this study is to investigate the SME in two typical protein based bio-polymers, namely nail and silkworm silk.

Unless otherwise stated, the strain and stress mentioned in this dissertation are engineering strain and stress.

1.3 Outline of the dissertation

Chapter 1 briefly introduces the concepts of shape memory effect and shape memory material. The objectives and outline of this study are presented.

Chapter 2 is a comprehensive review about various mechanisms in shape memory materials, current status of shape memory materials and some novel applications.

Chapter 3 reveals the underlying mechanism of the temperature memory effect (TME) in NiTi SMAs. Furthermore, the concept of TME is expanded and a new technique is identified, which has great potential for temperature sensor applications.

Chapter 4 demonstrates that the triple-SME is achievable in NiTi SMAs. The required conditions and mechanism are identified. The key parameters for optimization are discussed.

Chapter 5 systematically studies the SME in human nail keratin protein. Besides heat, water is proved to be a more effective stimulus for the SME. Heat and water may be combined to achieve the triple-SME.

Chapter 6 investigates silkworm silk following the similar approach as in chapter 5 to confirm that the SME is a common feature of this type of protein.

Chapter 7 summarizes the important conclusions of this study. Future works are proposed.

Chapter 2 Literature Review

In this chapter, a brief review of the current status of shape memory materials is presented, together with the underlying mechanisms behind the shape memory effect (SME). Besides the traditional thermally induced SME, some new features developed recently are summarized. Typical applications utilizing the SME are discussed.

2.1 Mechanisms of shape memory effect in shape memory materials

Although different types of shape memory materials may have different compositions and/or stimuli for the SME, their working mechanisms can be classified into three basic categories, as schematically illustrated in Figure 2.1, namely dual-state mechanism, dual-component mechanism and partial-transition mechanism [55, 56].

- Dual-state mechanism

Figure 2.1 (I-A) illustrates the working mechanism for thermally-induced SME in most SMAs. Taking NiTi SMA as an example, the material has two phases with different crystal structures and properties [57-60]. At high temperatures, a SMA is in the austenite phase and harder; while at low temperatures, it is martensite and relatively softer. The phase transformation from austenite to martensite upon cooling (thermally-induced) and/or stressing (stress-induced) is known as the forward martensitic transformation, which is *fully* reversible in SMAs [61, 62]. External stressing results in large deformation in a SMA by means of either phase transformation from austenite to martensite or martensite reorientation. Upon heating and/or removal of the stress, the SMA is able to transform back to austenite (known as the reverse martensitic transformation) and restores its original shape. The reversible

martensitic transformation and martensite reorientation are the underlying mechanisms for the thermally-induced SME in SMAs [25, 63, 64].

Figure 2.1 Basic working mechanism for SME. (I) Dual-state mechanism (DSM); (II) dual-component mechanism (DCM); (III) partial-transition mechanism (PTM). (1) Original shape; (2) after programming; (3) after shape recovery [56].

Figure 2.2 illustrates the lattice structure change in SMAs. At high temperatures, the SMA is in the austenite phase, which has a cubic lattice structure. Upon cooling without loading, it becomes twinned martensite, whose lattice structure is monoclinic. Martensite grows in a self-accommodate manner, so that up to 24 variants can be

formed [65]. Heating again will cause the transformation toward austenite again. If small volume difference and surface relief are ignored, virtually there is no shape change involved during this transition [66].

Figure 2.2 Illustration in change of lattice structure in SMAs [66].

At low temperatures, applying load will cause the reorientation of twinned martensite, which results in deformation associated with the detwinned martensite. Detwinned martensite can also transform into another detwinned martensite, which is not shown in Figure 2.2. Heating of detwinned martensite leads the phase transformation to austenite and SME is observed.

Besides loading at low temperatures, detwinned martensite can be derived from high temperature austenite at the presence of loading, too. If loading is removed, instant recovery is expected. This is called the super-elasticity [21, 67]. Super-elastic behavior is actually a kind of shape change effect.

Thermal properties of SMAs are characterized by four temperatures, namely martensite start temperature (M_s), martensite finish temperature (M_f), austenite start temperature (A_s) and austenite finish temperature (A_f). The former two indicate the temperature range for austenite to martensite transition and the latter two mark that for the reverse transformation. Figure 2.3 schematically shows the transformation temperatures of SMAs in a typical DSC cycle. Normally, M_s and A_f are not the same, and the difference is known as “hysteresis” [3, 68].

Figure 2.3 Schematic illustration of transformation temperatures of SMAs.

In some SMAs, there is an additional phase called “R-phase”, which appears upon cooling before martensite merges. R-phase is related to the rhombohedral distortion of the unit cell. Aging after solution treatment and annealing immediately after cold work are two effective ways to introduce R-phase [69-71].

Figure 2.1 (I-B) is for a shape memory material which can be triggered by applying an external field with particular direction. One example is the ferromagnetic SMA [28, 72-74]. The overall shape change may be the result of either reversible antiferromagnetic martensitic to ferromagnetic parent phase transformation, or rearrangement of two different martensite variants. Both are magnetic-field-induced.

Figure 2.1 (I-C) describes a kind of polymeric shape memory material that experiences the glass transition. Above the glass transition temperature (T_g), the polymer is soft and may be deformed easily; while below the T_g , the polymer is hard. Traditionally, these two states are named rubber state and glassy state, respectively. After being pre-deformed, the original shape may be recovered upon heating to above the T_g .

- Dual-component mechanism

As illustrated in Figure 2.1 (II), the structure of a shape memory material with DCM may be regarded as two segments or domains, one is matrix which serves as the elastic component, and the other is inclusion that serves as the transition component. The elasticity of elastic component is almost unaffected within the concerned working temperature range. However, the property of the transition component may be dramatically changed with the change of temperature due to the glass transition or melting, etc. Hence, at high temperatures, the material can be easily deformed. After subsequent cooling with constraint maintained, the transition component becomes hard again and thus prevents the elastic component from recovery. Consequently, the temporary shape is largely maintained after the constraint is removed. If the temperature rises again, the transition component softens again, and hence the elastic component is able to return to its original shape. Polyurethane is a typical shape memory polymer (SMP) under this category [30-32, 48, 75, 76].

Based on dual-component mechanism, a shape memory hybrid which is made of two materials without any SME as an individual, can be designed [6, 77]. In such a shape memory hybrid, one of the components serves as the elastic matrix and the other as the transition inclusion. The selection of components for shape memory hybrids is not

limited to polymers, but includes metals and organics as well. Ideally, it is expected that there is not any chemical interaction between the two components during fabrication so as to largely maintain the properties of individual materials. Consequently, the properties of a SMH can be easily predicted even in the early design stage.

- Partial-transition mechanism

Different from dual-state mechanism and dual-component mechanism, partial-transition mechanism is not an independent mechanism for the SME, but a rather special case which utilizes either dual-state mechanism or dual-component mechanism or a combination of both. Within an incomplete transition process, for instance, the glass transition or melting, part of the material is transformed and thus serves as the transition component while the remaining untransformed part serves as the elastic component. The programming temperature must be carefully controlled. Theoretically, partial-transition mechanism is not only applicable to polymeric materials but also metallic materials [78].

To order to characterize the SME properties of shape memory materials, a few standard terms have been defined in the literature. As illustrated in Figure 2.4, starting from the initial shape which is supposed to be strain/stress free, the material is deformed to a maximum strain of ε_L . After unloading, the residual strain is ε_U . Such a loading/unloading process is usually referred as programming. When the right stimulus is applied, the SME is triggered and the final shape has a strain of ε_R . This is the recovery process. The recoverable strain of a shape memory material is the difference between ε_U and ε_R . Table 2.1 lists the recoverable strain of a few typical shape memory materials.

Figure 2.4 Illustration of a SME cycle.

Table 2.1 Recoverable strain of typical shape memory materials.

Material	NiTi	CuZnAl	NiMnGa	Polyurethane	Polyethylene
Recoverable strain	8~9%	3~4%	9~10%	up to 400%	up to 1400%
References	[3, 21, 79]	[5]	[80, 81]	[39, 82]	[83]

Besides recoverable strain, shape fixity ratio R_f and shape recovery ratio R_r are important terms to evaluate the SME, where,

$$R_f = \frac{\varepsilon_U}{\varepsilon_L} \times 100\% \quad (2.1)$$

$$R_r = \frac{\varepsilon_U - \varepsilon_R}{\varepsilon_U} \times 100\% \quad (2.2)$$

2.2 Developments of shape memory materials

2.2.1 Multiple stimuli

In addition to direct heating to activate the SME, some other types of stimuli have been developed.

- Indirect heating

By adding in a proper amount of conductive/magnetic fillers into a thermo-responsive SMP, the resultant composite may be triggered by indirect heating via joule heating

and/or inductive heating [11, 41, 46, 47, 52, 53, 84-86]. Among them, carbon nanotubes [84, 87-89], carbon nanoparticles [90-92], and Ni powder [47] are some mostly used fillers. Light irradiation is another approach to activate thermo-responsive shape memory materials indirectly [93-95].

- Cooling

Based on the concept of dual-component mechanism, as an alternative to heating-induced one, cooling-induced SME has been realized. Sun *et al.* reported a silicone/tin hybrid that can be activated by either heating or cooling for shape recovery [1]. Tin is utilized as the transition component in this hybrid. Besides heating to melt tin for shape recovery, at around 13.2°C tin goes through the β -tin to α -tin transition, a phenomenon known as the “tin pest” [96], and consequently a piece of solid tin fractures into powder.

Wang *et al.* demonstrated that Poloxamer 407 (P407) is a more suitable material as the transition component for the cooling-induced SME [97]. The aqueous solution of P407 aggregates into solid form at around 35°C, and melts upon cooling to around 5°C.

- Water/moisture

Water/moisture induced-SME can be realized in a few different approaches. One is to change the relative relationship between the transition temperature of a shape memory material and the ambient temperature [48-50, 98, 99] via the plasticizing effect of water on the switching (transition) domain [100]. A decrease of T_g in polyurethane by more than 30°C is possible. Hence instead of heating to above its original T_g , upon immersing a piece of polyurethane in room temperature water, shape recovery can be

observed. It has been reported that water-induced SME is also applicable in hydrogel [101] and cotton cellulose nanowhiskers (CNWs) [102].

Another approach is to directly dissolve the transition component in water. Examples of such include sponge/cupric sulphate pentahydrate hybrid, silicone/sodium acetate trihydrate hybrid and polyhedral oligomeric silsesquioxane (POSS) molecules and poly(ethyleneglycol) copolymer, etc [13, 75, 97].

- Chemical

In addition to water/moisture, upon immersing in certain chemical solutions, chemical interaction or swelling effect [103] may cause a great change in the physical properties of a material, in particular in polymeric materials. Such a concept has been utilized for acetone [104] or N,N-Dimethyl formamide (DMF) [51] induced shape recovery in polystyrene (PS), and ethanol induced shape recovery in poly(methyl methacrylate) (PMMA) [105, 106].

- Light

Light-responsive SMPs are able for shape recovery upon exposing to light with a certain wavelength without causing any significant temperature fluctuation [44, 107-110]. The reversible change of crosslinking from photo-crosslinking to photo-cleaving is the underlying mechanism. Normally, light of different wavelengths is used for programming and shape recovery.

- Stressing

Ding reported a silicone-melting glue-sodium acetate trihydrate SMH that can be triggered by stressing [77]. Sodium acetate trihydrate has the super-cooling feature

that prevents it from transforming from liquid to solid even when temperature is actually below its normal crystallization temperature [111]. However, a gentle touching is able to initial the crystallization process. Significant latent heat released during crystallization can be used to trigger the thermally-induced SME in the hybrid. Besides, since solid sodium acetate trihydrate is fragile, impact induced shape recovery has been realized in silicone-sodium acetate trihydrate hybrid [77].

2.2.2 Triple-shape memory effect

If recovery is from a temporary shape to the original shape through one or more intermediate shape(s), this is the multiple-shape memory effect (multi-SME). As such, if there is only one intermediate shape, it is the triple-SME, while the traditional SME, which involves only two shapes, is the dual-SME.

It should be pointed out that the triple-SME is completely different from the two-way SME [3, 112], in which the material can switch between two shapes upon, for instance, thermal cycling. The two-way SME is actually a feature under the shape change effect, which is mentioned in Chapter 1. If only the permanent shape is memorized, this is the one-way SME as in traditional SME. To clarify, all SME discussed in this dissertation is strictly (one-way) shape memory effect.

Obviously, a shape memory material with the triple-SME is able to provide tremendous advantages. For instance, it is able to generate sophisticated motion in a pre-programmed manner to work as a machine [113]. A higher order of flexibility in such shape memory materials provides additional degree-of-freedom in design, which can significantly widen the application areas of shape memory materials.

The term of triple-SME is first introduced in SMPs. A polymer bilayer [114, 115] or a polymer with a gradient transition temperature [116] naturally has the ability for the

triple-SME. If a polymer system has two transition phases/segments with different transition temperatures, the triple-SME can be achieved after programming (Figure 2.5). The actual transition may be glass transition, melting, and nematic to isotropic state transition [117].

Figure 2.5 Triple-SME in D30N70/PCL upon heating [118].

Basically, there are three types of programming procedure for the triple-SME. In both Figure 2.6 (a) and (b), programming is in a two-steps manner. While the intermediate and the final temporary shape are introduced at two temperatures upon cooling in Figure 2.6 (a), these two shapes are programmed in two thermal cycles in Figure 2.6 (b). The former approach is applied in [115, 119-121], and in [117, 118], the latter approach is adopted. In Figure 2.6 (c), programming is done by one time deformation at one temperature [122, 123].

It should be emphasized that without further heating, the intermediate shape is able to be maintained there forever.

While the dual-SME and triple-SME are one-way SME, the two-way dual-SME and triple-SME reported in [124-126] are actually under the shape change effect.

Instead of two transitions, Xie demonstrated that perfluorosulphonic acid ionomer (PFSA), which has only one transition but over a wide temperature range, is capable for the multiple-SME [127]. The underlying mechanism for such a multiple-SME in polymers with one transition is revealed in [128], as a result of step-by-step release of the stored elastic energy in the elastic segment upon heating, so that one full transition

may be treated as a few small transitions. This is essentially the principle of PTM discussed in Section 2.1.

Figure 2.6 Three type of programming procedures for triple-SME in SMPs. Modified from [118].

While good progress has been observed in SMPs in recent years, the triple-SME in SMAs is hardly realized unless a gradient transformation temperature field is introduced, so that different parts have different transform temperatures. Instead of local annealing to permanently adjust the transition temperatures [129-131], a gradient transition temperature may be produced in a piece of SMA by pre-deformation at different strains [132]. As shown in Figure 2.7, the top part of a SMA strip is pre-bent more so that this part recovers at higher temperatures upon heating. Some special physical phenomena, such as buckling [133], may be applied for the triple-SME as well.

Figure 2.7 Sequential shape recovery of a pre-bent NiTi strip upon gradual heating [1].

So far there is no practically applicable approach to realize the triple-SME in SMAs for programming in a uniform manner, e.g., along the whole length of a piece of SMA.

2.2.3 Temperature memory effect in shape memory alloys

If heating is interrupted at T_s , which is between A_s and A_f , and followed by cooling to T_c , which is below M_f of a SMA, as shown in Figure 2.8, in the next round of heating process, an additional trough, which is closely related to T_s , appears in the differential scanning calorimeter (DSC) curve. Since the previous heating stop temperature is seemingly “memorized” by the material, this phenomenon is named as the temperature memory effect (TME). In the literature, it has also been referred as the “thermal arrest memory effect” [134] or “step-wise martensite to austenite reversible transformation” [135].

Figure 2.8 Illustration of TME in a thermal cycle. Black solid line: full cycle without interruption; grey dashed line: thermal path to induce TME.

Figure 2.9 presents a typical DSC curve of a NiTi SMA with single stop at 59°C, which is between A_s and A_f of this material, in the previous heating process. An additional trough appears in the final heating process. More interestingly, the peak temperature of the newly formed trough (T_p) is always 3~5 °C higher than the corresponding T_s in the previous heating process [136]. The actual temperature difference between T_p and T_s may vary with materials, but it is roughly a constant for a particular SMA. For instance, the gap for tested material shown in Figure 2.9 is always around 3.5°C.

Figure 2.9 DSC curve showing the TME in NiTi SMA with single stop in previous heating process. M1 and M2 represent different martensite.

Obviously, only part of martensite is transformed into austenite when heating is stopped at T_s , since it is between A_s and A_f . We may name the remaining martensite as M1. In the subsequent cooling to below M_f , M1 remains unchanged, while austenite transforms back into martensite. We name this part of martensite as M2. The volume fraction ratio between M1 and M2 is determined by T_s . A higher T_s results more M2. In Figure 2.9, the first trough at a lower temperature range is for the transformation of M2 to austenite, and the second trough is for the transformation from M1 to austenite.

The multiple TME as shown in Figure 2.10 can be achieved by conducting a series of interruptions at a few stop temperatures [137]. The NiTi SMA, which is the same as that in Figure 2.9, is subject to a first stop at 61 °C upon heating, followed by cooling below M_f . Same procedure is repeated twice, and second and third heating are stopped at 59 °C and 57 °C, respectively. After these procedures, in the final heating process, four troughs appear. The trough with the highest T_p corresponds to the first stop at 61 °C. The trough next to it corresponds to the second stop at 59 °C, and the next trough corresponds to the third stop at 57 °C. T_p of above new trough is about 3.5 °C higher than the corresponding T_s . This agrees with previous result presented in Figure 2.9.

Figure 2.10 DSC curve showing TME in a NiTi SMA after multiple stops.

It is possible to have N troughs as long as applied N stop temperatures follow a decreasing order [138]. With the increase of N , temperature range of the reverse martensitic transformation in final heating becomes wider [139].

The TME was first found in NiTi SMA, and then in NiTiX [140, 141], and in CuAlNi single crystalline and CuZnAl polycrystalline [142]. It turns out that the TME should be another common feature of SMAs.

So far the exact mechanism for the TME in SMA is still not quite clear. It is generally agreed that upon cooling M2 nucleates and grows within austenite, rather than expanding from existing M1 [143]. However, the actual reason why M1 and M2 transform to austenite separately is still an issue under debating. Madangopal *et al.* proposed that M2 has more elastic energy, which is the driven force for the reverse transformation, so that the transformation of M2 to austenite is somehow pre-positioned [134]. Airoidi *et al.* claimed that M2 is lack of elastic energy, and thus higher temperature is required for transformation [144]. It seems that neither explanation is supported by experimental evidence. It is also suggested that the elastic energy of M1 at the interphase is released during the formation of M2, which attributes to the rise of the transition temperature of M1 [145]. Further experimental verification is still required.

A phenomenological model has been developed to reproduce all observed phenomena of TME [146]. Quantitatively analysis has been performed to find the relationship between the number of interruptions and the transformed martensite fraction under various conditions [147].

The TME in SMAs without cold working is a one-time phenomenon. After cold working, the TME may remain in a couple of thermal cycles. Cold rolling also helps to widen the transformation temperature range for the TME [43]. The TME becomes more significant with repeated number of interruptions at the same heating stop temperature [148].

Instead of memorizing the previously stop temperature, stress induced memory effect memorizes the interrupted stress in the previous unloading process, known as “Incomplete cycle on recovery” [144, 149].

The TME in polymers is based on a totally different mechanism. The fundamentals and potential applications have been well explored [128, 150], and thus the TME in polymers is excluded from the scope of this dissertation.

2.3 Natural biomaterials as potential shape memory material

In addition to develop new shape memory materials, to enable the SME in existing materials is another approach, which may be acceptable by the industry. Bio-based polymer (also referred as bio-plastic in many occasions) is one prospective choice to take over the place of current plastics made from petroleum, which is going to be exhausted very soon [151, 152]. It is believed that bio-plastic will largely promote the development of green industry since traditional plastics may cause serious environmental problems. Particularly, it has been found that polylactic acid (PLA) based bio-plastic can have excellent SME [153-155]. PLA can be mass produced via the fermentation of renewable resources like corn starch or sugarcane [156], thus provides a feasible solution to such concern.

Thibaut *et al.* investigated the structure of human hair, the main component of which is keratin protein, and suggested that hair fiber may have the shape memory effect [157], but without any experimental evidence. According to Wortmann [158], keratin fibers, such as hair and wool, have a structure of intermediate filaments embedded in a matrix. Such two-phase intermediate filaments/matrix model was first proposed by Feughelman [159], later verified via transmission electron microscopy observation by Rogers [160]. Figure 2.11 schematically illustrates the morphological structure of a typical α -keratinous fiber, in which inset is the simplified model developed in [159].

Figure 2.11 Morphological structure of α -keratinous fiber [158].

Intermediate filaments provide structural support to the cell. It comprises type I (28 members) and type II (26 members) genes, which is located at the long arm of human chromosome 17 and 12, respectively [161]. An illustration of the tripartite domain structure of keratin intermediate filaments and its electron micrograph image are shown in Figure 2.12.

In the intermediate filaments/matrix model, the matrix is mainly consisted of non-crystalline component, which is accessible to water. It has been found that the modulus of matrix decreases significantly at the presence of moisture [159, 163], and such a phenomenon is attributed to the strong plasticizing effect of water on matrix [164-167]. In the contrast, the intermediate filaments contains α -helical component and is highly organized [168]. Even under harsh conditions, the intermediate filaments does not interact with water and its modulus remains the same [166, 168]. As such, based on the concept of dual-component mechanism, it is possible to enable the SME in keratin materials.

Figure 2.12 Illustration of microstructure of keratin intermediate filaments. (a) Tripartite domain structure of keratin proteins; (b) electron micrograph of negatively stained filaments reconstituted in Vitro from purified human K5 and K14 proteins; (c) organization of keratin filaments via indirect immunofluorescence of primary mouse skin keratinocyte cultures [162].

It has been reported that after severe torsion, the dragline spider silk, which is a kind of β -keratin with β -pleated sheets twisted together [169-171], can gradually recover its original shape without external stimulus [172, 173]. Such phenomenon is actually a kind of viscous-elastic behavior rather than standard shape memory phenomenon as claimed in Chapter 1.

2.4 Typical applications of shape memory materials

A wide range of applications have been proposed and realized even since the discovery of the SME. One may refer to [3, 7, 21, 54, 79, 108, 174-177] for

comprehensive reviews of applications of shape memory materials in the past years. In this section, only a few typical and novel applications developed recently are presented.

- Bio-medical applications

Shape memory medical devices can be compressed or folded into a temporary shape with a much smaller size before being implanted inside the body of a patient. This allows minimal invasive surgery which can remarkably reduce the pain and curing time for patients.

Deployment of such devices may be triggered by body temperature (or other means of direct/indirect heating) or a specific stimulus. Hence, stents [178-184] and catheters [185-189] made of shape memory materials can be conveniently deployed through a small surgical cut. Moreover, if a shape memory material is programmed with the triple-SME, removal of the implanted devices is also achievable via the same minimal invasive approach, but in a reverse manner.

Suture is used to hold the wound tissue together in medical operations. With a suture made of SMP [54, 190, 191], the time-consuming stitching and knotting process can be largely avoided by means of triggering the SME for self-tightening function. Sutures made of biodegradable SMPs have the additional biodegradation function [39, 54].

- Active disassembly

Disassembly of obsolete products is essential for effective recycling and reuse. Since manual disassembly is highly labor intensive, active disassembly is more efficient for massive operation.

Active disassembly using shape memory materials has been proposed [1, 192, 193]. Screw, joint, snap-fit and tab made of shape memory materials are demonstrated for active disassembly without any physical touch [1, 192, 193].

- Surface patterning

The SME enables the appearance and disappearance of a surface pattern atop shape memory materials, which may be utilized in anti-counterfeit applications. As shown in Figure 2.13, a piece of polystyrene programmed with the triple-SME is able to show two different surface patterns upon step-by-step heating. Upon heating to lower temperatures, the surface pattern changes from one to the other side of a coin. The surface pattern disappears upon further heating to higher temperatures.

Figure 2.13 Demonstration of step-by-step change in surface pattern upon heating in polystyrene SMP [194].

By coating a thin layer of gold atop a pre-strained SMP substrate, different patterns of micro/ nano sized wrinkles can be produced after heating for shape recovery [195, 196]. The SME in SMP and difference in thermal expansion coefficient between coating and substrate are the key factors for wrinkle generation.

Chapter 3 Temperature Memory Effect in NiTi Shape Memory Alloys and Sensor Applications

Besides the well-known shape memory effect (SME), the temperature memory effect (TME) is another feature of shape memory alloys (SMAs) associated with the reversible martensitic transformation. Different from that in the SME, in which the original shape is remembered, a particular temperature is somehow memorized in the TME.

In this chapter, we investigate the underlying mechanism (from the energy point of view) behind the TME via a series of differential scanning calorimeter (DSC) tests, and then demonstrate the feasibility of utilizing the modified TME for temperature sensors to monitor the over-heating temperature. Different patterns are obtained by altering programming parameters, and thus, we obtain a complete picture to reveal the relationship between interruption temperature and resulted recovery sequence.

3.1 Mechanism of temperature memory effect

Although the temperature memory effect (TME) has been discovered for some years, the exact mechanism is still unclear so far. According to the literature, M1 and M2 are used to denote the original martensite and newly formed martensite in an interrupted thermal cycle, respectively [143]. More precise speaking, both M1 and M2 are martensite variant groups, which are formed to effectively minimize the elastic energy in a SMA. Since M2 is produced from austenite directly instead of being extended from the existing M1, there is an interface between M1 and M2. It is believed that the release of elastic energy at the interface of M1 and M2 is the major reason for the

TME [143]. However, the underlying mechanism for the two separate troughs in the DSC curve in the final heating process is yet fully understood.

3.1.1 Experimental and results

A series of DSC tests were conducted on a commercial 0.2 mm diameter $\text{Ni}_{55.3}\text{Ti}_{44.7}$ wire, which was bought from Image SI Inc, USA. As-received material was pre-annealed at 800°C for one hour followed by quenching in iced water. A TA Instrument DSC Q200 was used for all DSC tests at a heating/cooling rate of 10°C/min. Typical result of a full thermal cycle between 0°C and 85°C is presented in Figure 3.1(a).

Figure 3.1 Typical DSC results of $\text{Ni}_{55.3}\text{Ti}_{44.7}$ wire. (a) Full thermal cycle; (b) and (c) typical testing results for the TME (grey line: result of previous process, if applicable; dark line: result of current process).

In the single interruption TME test (as in Figure 3.1b), the thermal cycle was started at 85°C, which is higher than A_f of the sample; then it was subject to cooling until temperature dropped to 0°C, which is lower than M_f , to ensure a complete forward martensitic transformation. After that, heating was stopped at a particular temperature, namely T_s , such that the reverse martensitic transformation was interrupted at a certain martensite fraction. Subsequently, cooling back to 0°C was applied again, followed by heating to 85°C, which ended a full cycle of TME.

As shown in Figure 3.1(c), two separate troughs instead of only one appear in the final heating curve, which reveals the well-known TME. We make the following definitions: Q_i ($i=A, M, 1\sim4$), are heat generated or absorbed during forward or reverse martensitic transformation, which can be calculated by integrating the respective area as shown in Figure 3.1, where:

- Q_A and Q_M denote the energy associated with M-A and A-M transition in a full thermal cycle without any interruption (Figure 3.1a);
- Q_1 and Q_2 denote the energy associated with a partial M-A and A-M transition when a single interruption is applied (Figure 3.1b);
- Q_3 and Q_4 denote the energy associated with the first and second stage of M-A transition in the final heating process (Figure 3.1c).

In above definitions, M and A stands for martensite and austenite, respectively. We further define $\xi_r=Q_1/Q_A$, which denotes martensite fraction, and also $\xi_f=Q_2/Q_M$, which will be discussed later.

Table 3.1 lists experimental results in a series of TME tests at different ξ_r s. For easier comparison, normalized values are used instead of absolute values. Within the accepted error range, we may conclude that: $Q_1\approx Q_3$, $Q_3+Q_4\approx Q_A$, for all different ξ_r s.

Table 3.1 Experimental results of TME at different ξ_r s.

ξ_r (Q_1/Q_A)	ξ_f (Q_2/Q_M)	Q_M/Q_A	Q_2/Q_A	Q_3/Q_A	Q_4/Q_A	$(Q_3+Q_4-Q_A)/Q_A$
97.3%	90.3%	82.9%	74.9%	98.1%	2.7%	0.9%
90.7%	79.6%	83.8%	66.8%	94.1%	10.5%	4.6%
73.5%	63.8%	87.3%	55.7%	72.2%	28.7%	0.9%
63.2%	44.4%	87.9%	39.0%	61.8%	38.3%	0.1%
57.9%	42.8%	84.0%	36.0%	58.0%	42.8%	0.8%
50.2%	35.1%	82.6%	29.0%	53.6%	50.0%	3.6%
40.8%	14.3%	83.6%	12.0%	39.4%	62.7%	2.1%
31.6%	6.8%	83.2%	5.7%	30.8%	72.8%	3.7%
25.8%	5.6%	83.5%	4.7%	26.6%	76.6%	3.2%
20.9%	2.9%	82.1%	2.4%	22.9%	78.7%	1.6%
8.7%	0.0%	80.8%	0.0%	8.3%	94.0%	2.3%
2.6%	0.0%	82.4%	0.0%	2.4%	101.7%	4.1%

3.1.2 Energy variation in an interrupted martensitic transformation

Three types of energy contribute to the trough (Q_A) and peak (Q_M) monitored by DSC instrument [61, 62], and

$$-Q_M = -\Delta H_{ch}^{A-M} + \Delta H_{el}^{A-M} + E_{fr}^{A-M} \quad (3.1)$$

$$Q_A = \Delta H_{ch}^{M-A} - \Delta H_{el}^{M-A} + E_{fr}^{M-A} \quad (3.2)$$

where ΔH_{ch} represents the chemical free energy, ΔH_{el} represents the elastic energy, E_{fr} represents the energy dissipation. Herein symbols A and M stand for austenite and martensite, and superscript A-M denotes the forward martensitic transformation and M-A denotes the reverse martensitic transformation. The quantities in Eqns (3.1) and (3.2) are absolute value. A negative sign indicates energy absorption, and a positive sign indicates energy release, hereinafter.

Here, ΔH_{ch} , which is more or less temperature dependent, is not affected by any temperature interruption; ΔH_{el} is stored during the forward transformation and serves

as the driving force for the reverse transformation; E_{fr} is due to friction and/or any other types of energy dissipation in a transformation.

For simplicity, we may assume that $\Delta H_{el}^{A-M} = \Delta H_{el}^{M-A}$ and $\Delta H_{ch}^{M-A} = \Delta H_{ch}^{A-M}$, and ignore the difference of heat capacity between austenite and martensite. Thus, $Q_A - Q_M = E_{fr}^{A-M} + E_{fr}^{M-A}$ [61, 62]. Moreover, it is usually assumed that E_{fr}^{A-M} and E_{fr}^{M-A} are linear functions of ξ_r , and $E_{fr}^{A-M} = E_{fr}^{M-A}$.

In the final heating process, the M-A transformation is in a two steps manner if a single interruption is applied previously: the first trough is for M2 (Q_3 in Figure 3.1c), while the second one is for M1 (Q_4 in Figure 3.1c). According to Table 3.1, $Q_3 + Q_4 \approx Q_A$. Thus we may conclude that no additional energy dissipation is involved during the whole process of TME. On the other side, the chemical energy, i.e., Gibbs free energy of martensite and austenite, which is mainly determined by temperature, is not affected. Therefore, the change of the pattern of DSC curve should be largely due to the re-distribution of elastic energy.

Consider a full thermal cycle without any interruption. Starting from a nuclei, martensite grows gradually in a self-accommodate manner upon cooling, and elastic energy is accumulated. Martensite that transforms at lower temperatures is associated with a higher elastic energy. Upon heating, the stored elastic energy serves as the driving force and thus promotes the M-A transformation. That is the reason why the latter formed martensite in the A-M transformation transforms earlier in the M-A transformation [63-65], as schematically illustrated in Figure 3.2(a). We use a scale from 0 to 1, to distinguish different martensite parts with different levels of elastic energy, where 0 stands for the lowest elastic energy and 1 stands for the largest. It

should be noted that the grid area shown in Figure 3.2 stands only for part of martensite with the same elastic energy value in the unit of J/g.

Figure 3.2 Schematic illustration of TME under different conditions. (a) Complete cycle without interruption; (b) heating stopped at T_s ; (c1) hypothesis curve upon heating, M1 and M2 separated; (c2) hypothesis curve upon heating, M1 and M2 combined; (c3) experimental curve upon heating.

Consider the case of single interruption TME. The M-A transition is stopped at T_s , where the elastic energy at the interface of austenite (which later on transforms into M2) and M1 is assumed to be 0.3, as in Figure 3.2(b). It is currently believed that upon cooling, M2 grows from nucleation inside austenite instead of expanding from existing M1 [143]. We made an assumption that the growth of M2 starts from 0 elastic energy, as in a normal cycle without interruption (Figure 3.2a), therefore the final heating curve for M2 should form a shape as illustrated in Figure 3.2(c1), i.e., throughout $[A_s, A_f]$, only with a lower magnitude. While part of the elastic energy in M1 near the interface has been released during the formation of M2, the curve for M1 in the final heating process should be re-shaped as illustrated in Figure 3.2(c1), within $[T_s, A_f]$. Based on above assumption, if we overlap these two parts together, the combined DSC curve in the final heating process should be more or less in a shape as

shown in Figure 3.2(c2), which does not agree with the experimental result shown in Figure 3.2(c3). Hence the preceding assumption is not valid.

On the other hand, $Q_1 \approx Q_3$, i.e., the majority of M2 has transformed into austenite within $[A_s, T_s]$. Therefore, the elastic energy of M2 should be between 1 and 0.3 (from A_s to T_s). The experimental results indicate that M2 has almost the same level of elastic energy before and after interruption, which implies that some kind of inheritance is built up during its formation. One possible explanation is that when M2 nucleates, it must nucleate from exactly where the interface is, and inherit or absorb the elastic energy already stored there (i.e., 0.3 in this particular case) instead of starting from 0 as in normal case without interruption. This is reasonable as martensite always tends to nucleate from a non-equilibrium point. As compared with elsewhere deep inside austenite, M2 is more likely to start at the boundary.

The newly formed M2 also grows in a self-accommodate manner. Hence the DSC curve of the first transformation step in the final heating process is in a full trough style. Since the boundary area of M1 loses a little bit of elastic energy, e.g., decreased from 0.3 to 0.2, due to the formation of M2 (possibly this part of elastic energy transfers from M1 to M2 through interface), a higher temperature is required in order to complete the transformation in this area. As a result, DSC curve of the second transformation step becomes sharper than the original one, since the fraction with the same level of elastic energy increases.

According to Table 3.1, it is noted that apparently ξ_f is always smaller than ξ_r . If ξ_f against ξ_r is plotted as shown in Figure 3.3, we can see that above 20% ξ_r , ξ_f is about a linear function of ξ_r , but with a slope larger than 1. Hence the difference between ξ_f and ξ_r decreases with the increase of ξ_r . If ξ_r drops from 20%, ξ_f quickly approaches 0.

It is almost a straight line in the DSC curve without any visible peak, as shown in Figure 3.4. The trend does not follow 1:1 for $\xi_f = \xi_r$. It is also observed in Figure 3.4 that the peak temperature, together with the apparent M_s , decreases with the decrease of ξ_r .

Figure 3.3 Plot of ξ_f against ξ_r . Grey dashed line is for $y=x$ for easy comparison.

Figure 3.4 Typical DSC curves of A-M transformation after interruption with different ξ_r s.

The seemingly unusual relationship between ξ_r and ξ_f is another evidence to confirm that M2 starts with the same level of elastic energy as that of the interface. Earlier

interruption results in a smaller ξ_r , and thus a higher average elastic energy in M2. Hence more chemical energy is converted into elastic energy during the cooling process, and less heat is released and detected by DSC. If ξ_r is low enough, e.g., less than about 20%, almost all chemical energy is converted into elastic energy, so that almost no heat is released at all. Consequently, a peak is effectively reduced into a straight line. The shift of the apparent M_s is due to the same reason, as a higher chemical energy is required by means of overcooling for the growth of martensite. It should be pointed out that although it is not so easy to spot in the DSC curve, the A-M transition does start below A_s . If cooling is stopped at 25°C instead of 0°C for the case of 9% ξ_r as shown in Figure 3.4, there is still a small trough in the following heating DSC curve, which indicates that M2 has been transformed from austenite.

Figure 3.5 schematically illustrates the elastic energy in the TME. For a full thermal cycle (Figure 3.5c), elastic energy is accumulated upon cooling, and the part with the highest elastic energy is the first part to transform back upon heating. If M-A transformation is interrupted (Figure 3.5b), the subsequent A-M transformation starts at the interface with the same elastic energy as that of the interface (dashed line) rather than 0. With the decrease of ξ_r , the apparent M_s also decreases accordingly, due to the lack of chemical energy. On the other hand, since more chemical energy is converted and stored as elastic energy, while dissipation remains the same, less heat is released and detected. In the final heating process, the re-distributed elastic energy determines the shape of two separate troughs and the temperature gap between them.

Figure 3.5 Schematic illustration of elastic energy in the TME. Horizontal axis represents temperature and vertical axis represents elastic energy.

It should take note that the nucleation of martensite right at M-A interface upon cooling does not contradict with the previous hypothesis that M1 and M2 have different orientations [143, 145]. The formation of M2 nucleus is a completely new one. Since M2 is independent on M1, the orientation of M2 is not necessarily to be the same as M1.

3.2 NiTi SMA based temperature sensors

Given the nature of temperature dependence of the TME, applications of the TME in temperature monitoring and recording are expected. In fact, in many applications, such as cold chain logistics, it is required to monitor if individual items (instead of a whole box of them) have ever been overheated and what the highest temperature was if over-heating did happen. Since electronic sensors are complicated and require power supply, a cost effective alternative is highly in demand at present.

A few attempts have been made based on the SME in NiTi SMAs [197-200]. However, for a particular NiTi SMA, the actual shape during the martensitic

transformation is not only determined by the exact temperature, but also the real strain/stress distribution after pre-deformation. As well known, pre-straining does have remarkable influence on the transition temperature in NiTi SMAs [132]. Hence, the reliability of such temperature sensors is limited. Such problems may be avoided by utilizing the TME instead, where there is no macroscopic shape change involved.

In addition to $\text{Ni}_{55.3}\text{Ti}_{44.7}$ wire tested above, we also tested $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon with a cross section of $2 \times 0.2 \text{ mm}^2$, provided by Mide Technology Corporation, USA. In each thermal cycle, T_s denotes the interruption temperature during the previous heating process as usual, and T_c denotes the lowest temperature reached during the cooling process. Our focus is on the gap between the highest temperature ever reaches in the previous thermal cycles and the trough in the final heating process.

By means of exploring beyond the limit in the conventional TME, i.e., the requirement of cooling to below martensitic finish temperature (M_f) in each thermal cycle, we investigated two other situations, one is cooling to between M_f and martensite start temperature (M_s), and the other is cooling stopped above M_s .

Herein, the conventional TME, in which T_c is always below M_f , is defined as c-TME; while the modified one is referred as m-TME I, if T_c is between M_f and M_s , or m-TME II if T_c is above M_s .

Typical result of a full temperature range DSC cycle is plotted in Figure 3.6. Accordingly, we conducted a series of tests for c-TME, m-TME I and m-TME II on both types of SMAs. All DSC tests were started at 100°C , which is higher than A_f of both SMAs and then cooled to 0°C to ensure almost complete forward martensitic transformation. In the following thermal cycle, heating was stopped at T_s , which is within the transition range from martensite to austenite, followed by cooling to a

specific T_c . Such a kind of thermal cycling might be repeated a few times with predetermined T_s and T_c in each cycle, before the sample was finally heated to 100°C . Unless otherwise stated, the heating/cooling rate was always $10^\circ\text{C}/\text{min}$ hereinafter.

Figure 3.6 Full temperature range DSC results. (a) $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon; (b) $\text{Ni}_{55.3}\text{Ti}_{44.7}$ wire.

For convenience, in all DSC curves presented here, dashed grey line is for the previous thermal cycle, solid black line represents the result in the final heating process, and solid grey line is for the result of a full range thermal cycling without interruption (i.e., the results plotted in Figure 3.6).

3.2.1 Conventional-temperature memory effect

We started with the simplest case of single-stop c-TME. Figure 3.7 shows a typical c-TME curve for $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon in which T_s is 59.4°C . Note that as shown in Figure 3.7, we define the start temperature of the second trough as T_t , and the temperature gap between T_t and T_s as T_G . A close-look reveals that T_G is about 3.3°C in this particular test.

Figure 3.7 Typical DSC curve of single-stop c-TME for $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon with T_s at 59.4°C .

Our interest is focused on the situation that temperature fluctuation is in a random fashion without any pattern to follow. We may treat the case of random temperature fluctuation as a series of single-stop cases. As a matter of fact, all kinds of single-stop cases can be classified into two types, depending on whether current T_s is higher or lower than the previous highest temperature (T_h). If current T_s is higher than the previous T_h , current T_s becomes the updated T_h ; otherwise, T_h remains unchanged.

Note that our concern is the overall T_h [i.e., $\max(T_{si})$, where $i=1,2,\dots$] within the whole temperature fluctuation period, and our aim in this study is to estimate T_h based on the DSC result of the (final) heating test. It should be noted that symbol T_G specially refers to the gap corresponding to T_h , while T_{Gi} is for individual T_{si} . Obviously, T_G is updated with the updating of T_h .

Figure 3.8 shows typical DSC curves of double-stop c-TME in $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon. Note that numbers 1 and 2 marked in Figure 3.8 are used as subscripts herein to represent the first stop and second stop, respectively. Detailed testing parameters and

key results are listed in Table 3.2, in which numbers highlighted in bold are T_h [$\max(T_{si})$, where $i=1,2$] and T_G (corresponding to the trough at a higher temperature) of each test. It is revealed that if T_{s2} is higher than T_{s1} [Figure 3.8(a)(b) and (i-iv) in Table 3.2], there is only one new trough in the final heating process, although there are two stops. This is because the influence of the first stop has been largely eliminated by the second stop. T_G is largely dependent on the relative position of T_{s2} , i.e., the closer is T_{s2} to $T_{s1}+T_{G1}$, the smaller is the final T_G .

Figure 3.8 Typical DSC curves of double-stop c-TME for $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon. (a) and (b): $T_{s2} > T_{s1}$; (c) and (d): $T_{s2} < T_{s1}$.

A few typical cases of $T_{s2} < T_{s1}$ are revealed in Figure 3.8(c)(d) and (v-viii) in Table 3.2, in which there are two additional troughs in the final heating process. In most of the previous studies on c-TME, such as in [134, 138], the stop temperature in the following thermal cycle is always lower than the previous one(s) to avoid eliminating

the influence of the previous stop temperature(s). Although a lower T_{s2} does not affect the shape of the new trough corresponding to T_{s1} , it does affect T_{G1} (so that T_G as well) slightly. It can be seen that the closer is T_{s2} to T_{s1} , the larger becomes T_{G1} and T_{G2} , and vice versa.

Table 3.2 Testing parameters and results of double-stop c-TME for Ni_{55.8} Ti_{44.2} ribbon. Unit for temperature is °C.

	T_{s1}	T_{c1}	T_{s2}	T_{c2}	T_{G1}	T_{G2}	Reference figure
i	61.3	0	63.0	0	-	2.6	
ii	61.3	0	64.5	0	-	1.6	Figure 3.8 (a)
iii	61.3	0	65.6	0	2.9	3.3	
iv	61.3	0	67.3	0	3.1	4.0	Figure 3.8 (b)
v	61.3	0	59.9	0	4.6	3.8	Figure 3.8 (c)
vi	61.3	0	58.3	0	4.4	3.3	
vii	61.3	0	56.8	0	4.0	2.8	
viii	61.3	0	55.4	0	3.7	2.6	Figure 3.8 (d)

Based on Table 3.2, Figure 3.9 plots the relationship between T_G and T_{s2} . As we can see, for an unknown T_{s2} , there is no particular trend at all for T_G even T_{s1} is always fixed at 61.3°C. Since T_G may be anywhere between 1.6°C and 4.6°C according to the results of this set of tests, $T_h \in [T_t - 4.6^\circ\text{C}, T_t - 1.6^\circ\text{C}]$, i.e., within a temperature range of 3°C.

Figure 3.9 Relationship between T_G and T_{s2} for Ni_{55.8} Ti_{44.2} ribbon ($T_{s1}=61.3^\circ\text{C}$, double-stop c-TME).

3.2.2 Modified-temperature memory effect type I and type II

Three experiments were conducted using $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon and the results are plotted in Figure 3.10, in which the highest T_s is the same (59.4°C), but T_c is a variable. Refer to (i-iii) in Table 3.3 for testing parameters in individual tests. Note that in Figure 3.10(a), there are two thermal cycles, where the second one is between 48°C and 56°C , which is within $[M_s, T_h]$. In comparison with the result in Figure 3.7, where there is no second thermal cycle, we may conclude that as long as there is no further phase transformation in a thermal cycle within $[M_s, T_h]$, as shown here, there is not any significant change in the DSC curve of the final heating process and thus T_G remains the same. On the other hand, according to Table 3.3, with the increase of T_c , less austenite is transformed back into martensite, so that the amplitude of the first trough in the final heating process decreases. If T_c is above M_s , there is only one trough. In the meantime, T_G is reduced from 3.3°C (i in Table 3.3) to 0.9°C (iii in Table 3.3).

Figure 3.10 Typical DSC curves of TME for $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon, in which $T_s=59.4^\circ\text{C}$. (a) Lowest $T_c < M_f$, c-TME; (b) $M_f < T_c < M_s$, m-TME I; (c) $T_c > M_s$, m-TME II.

According to previous definitions, here (ii) in Table 3.3 is m-TME I and (iii) is m-TME II. As a matter of fact, in real practice, c-TME and m-TME I are most likely not applicable as the mechanism for a temperature sensor to capture the event of over-heating. Only m-TME II is achievable via selecting a SMA with the right M_s

according to the temperature condition(s) in a real application. Hence, in the following study, we only focus on m-TME II.

Table 3.3 Testing parameters and results of $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon ($T_s=59.4^\circ\text{C}$). Unit for temperature is $^\circ\text{C}$.

	T_{s1}	T_{c1}	T_{s2}	T_{c2}	T_G	Reference figure
i	59.4	48	56.4	0	3.3	Figure 3.10(a)
ii	59.4	24	-	-	2.2	Figure 3.10(b)
iii	59.4	48	-	-	0.9	Figure 3.10(c)

Some typical DSC results of m-TME II for $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon are presented in Figure 3.11. Detailed testing parameters and key results are listed in Table 3.4. Note that the lowest temperature in thermal cycling (i.e., T_{c1} and T_{c2}) was set to be 50°C to avoid thermally induced martensite.

Figure 3.11 Typical DSC results of m-TME II for $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon. (a) and (b): Single stop; (c) and (d): double-stop with increased T_s , and $T_{s2} - T_{s1} > T_{G1}$; (e) double-stop with decreased T_s ; (f) double-stop with increased T_s , and $T_{s2} - T_{s1} < T_{G1}$.

Table 3.4 Testing parameters and key results of m-TME II for Ni_{55.8}Ti_{44.2} ribbon.
Unit for temperature is °C.

		T _{s1}	T _{c1}	T _{s2}	T _{c2}	T _{G1}	T _{G2}	Remark
Single arrest	i	55.0	50	-	-	0.7	-	Figure 3.11(a)
	ii	58.0	50	-	-	0.8	-	
	iii	61.0	50	-	-	0.9	-	
	iv	64.0	50	-	-	1.1	-	Figure 3.11(b)
	v	67.0	50	-	-	1.6	-	
	vi	70.0	50	-	-	1.7	-	
Double arrest	vii	58.0	50	60.0	50	0.8	0.9	Figure 3.11(c)
	viii	58.0	50	62.0	50	0.8	1.0	
	ix	58.0	50	64.0	50	0.8	1.2	
	x	58.0	50	66.0	50	0.9	1.5	Figure 3.11(d)
	xi	63.0	50	60.0	50	1.1	-	Figure 3.11(e)
	xii	58.0	50	58.5	50	-	0.5	Figure 3.11(f)

As that in c-TME, after one stop, the reverse martensitic transformation only starts at above T_s. However, when compared with that in c-TME,

- The actual over-heating temperature for the transformation to start is much less;
- Combining the grey dashed line (previous heating) and black solid line (final heating) together results in a profile which approximately fits into the grey solid line (envelop of the DSC curve of a full thermal cycle).

Unlike that in c-TME (Figure 3.8), there is no austenite transforming back to martensite during cooling in m-TME II. Hence there is only one trough in the final heating process. After reaching the bottom of trough, the DSC curve essentially follows that of the full thermal cycle. Since there is only one trough, we can ignore those small fluctuations as revealed in Figure 3.11(c) and (f).

Closely examining (i-vi) in Table 3.4 reveals that T_G increases with the increase of T_{s1} . By comparing (iii) and (viii), (iv) and (ix), (v) and (x) in Table 3.4, we may conclude that T_G is only dependent on T_h . In other words, as long as T_h is not surpassed, regardless of the actual type of thermal cycling experienced, the final heating curve remains the same. This is different from that in c-TME, in which, T_s , if lower than T_h , affects the final T_G .

Now let us take a look the situation when $T_{s2} - T_{s1} < T_{G1}$. According to (ii) in Table 3.4, if T_{s1} is 58.0°C, T_{G1} is expected to be about 0.8°C. If we set T_{s2} to be within $[T_{s1}, T_{s1} + T_{G1}]$, e.g., 58.5°C as shown in Figure 3.11(f) and (xii) in Table 3.4, the final T_G is found to be 0.5°C only. This is a special situation in m-TME II, i.e., as long as the following T_s does not exceed the previous $T_h + T_G$, T_t in the final heating process is still associated with the previous T_h (other than the new T_s). In other words, in order to erase the influence of previous T_h , new T_s has to be higher than $T_h + T_G$. If not, T_t corresponding to the previous T_h remains almost unchanged, which results in a smaller gap in the final heating process. As such, $T_h \in [T_t - T_G, T_t]$, which gives an error of $\pm T_G/2$; while in the normal situations, $T_h = T_t - T_G$.

Same as that in c-TME, m-TME II is also achievable in a range of NiTi SMAs. We have obtained similar results for Ni_{55.3}Ti_{44.7} wire (see Figure 3.12 and Table 3.5). It is confirmed that the range of T_h can be estimated based on the final heating result of DSC test, i.e., $T_h \in [T_t - T_G, T_t]$.

Figure 3.12 Typical DSC curve of m-TME II for $\text{Ni}_{55.3}\text{Ti}_{44.7}$ wire. (a) and (b): Single stop; (c) and (d): double-stop; (e) and (f): triple-stop.

Table 3.5 Testing parameters and results of m-TME II for $\text{Ni}_{55.3}\text{Ti}_{44.7}$ wire. Unit for temperature is $^{\circ}\text{C}$.

		T_{s1}	T_{c1}	T_{s2}	T_{c2}	T_{s3}	T_{c3}	T_{G1}	T_{G2}	T_{G3}	Reference
Single-stop	i	47.0	45					1.0			
	ii	51.0	45					1.1			
	iii	55.0	45					1.0			Figure 3.12 (a)
	iv	59.0	45					1.1			
	v	63.0	45					1.7			
	vi	67.0	45					1.8			Figure 3.12 (b)
Double-stop	vii	55.0	45	59.0	45			1.0	1.2		Figure 3.12 (c)
	viii	55.0	45	63.0	45			0.9	1.7		
	ix	55.0	45	67.0	45			0.9	1.7		
	x	63.0	45	59.0	45			1.7			Figure 3.12 (d)
Triple-stop	xi	55.0	45	67.0	45	58.0	45	0.9	1.7		Figure 3.12 (e)
	xii	55.0	45	67.0	45	68.0	45	0.9		1.0	Figure 3.12 (f)

As discussed in Section 3.1.2, the temperature gap in c-TME is largely due to the re-distribution of elastic energy at the interface of martensite and austenite when the forward martensitic transformation starts upon cooling [143, 201]. As for m-TME II, since cooling is stopped above M_s , no forward martensitic transformation is involved

at all, and the only phase transition in m-TME II should be the reverse martensitic transformation, which may have been interrupted once or several times. Therefore the re-distribution of elastic energy should not happen. The pattern of the newly formed trough also confirms such inference, since the reverse transformation is merely delayed, while all major features are largely maintained.

In the absence of any kind of interruption, M_s and A_f of a NiTi SMA should be different due to hysteresis. The hysteresis in NiTi SMA is mainly due to internal friction, plus dislocation and/or slip during the growth or shrinkage of martensite. In order to overcome such resistance, further transformation must start at a higher temperature for a larger difference in chemical energy. If temperature increases continuously, the transformation proceeds till it is finished. However, if heating is stopped before transformation is completed, the interface of martensite and austenite serves as an additional energy barrier to overcome before further transition happens. This is the basic underlying mechanism for the m-TME II and corresponding T_G .

3.2.3 Temperature sensor based on modified-temperature memory effect II

As reported in the literature, the temperature gap could be reduced up to 0.1°C by applying a high pre-load and using constrained heating for c-TME [143]. However, from practical point of view, neither c-TME or m-TME I is suitable for temperature sensors as both of them require cooling below a certain temperature (M_f or M_s) in every thermal cycle, which is almost impossible in real practice.

Based on above investigations, it seems that we may choose a NiTi SMA with its M_s lower than that can ever be reached in an actual application, and follow m-TME II to monitor over-heating event. Figure 3.13 presents the relationship between T_G and T_t of both tested materials following m-TME II. For a particular SMA selected, since T_G

is determined by T_h , we only need to conduct a series of single-stop tests with a certain interval of T_s to establish such a relationship. No matter how complicated the actual temperature fluctuation is in a real situation, T_h can always be estimated based on this relationship, since $T_h \in [T_t - T_G, T_t]$, where T_G is dependent on the exact T_t . As Figure 3.13 reveals, T_G increases remarkably when T_t is closer to A_f , which indicates that the temperature range close to A_s should be used for better precision.

Figure 3.13. Relationship between T_G and T_t based on m-TME II.

The application procedure of SMA temperature sensors based on m-TME II is summarized as following. An illustration is shown in Figure 3.14.

- 1) Find the minimal temperature ($T_{\min}$) which may happen and the over-heating temperature range for monitoring (i.e., the lower limit temperature, T_{low} , and the upper limit temperature, T_{upp}) in a real application;
- 2) Select a NiTi SMA with $M_s < T_{\min}$, $A_s = T_{\text{low}}$, and $A_f > T_{\text{upp}}$. We may further choose $(A_s + A_f)/2 > T_{\text{upp}}$ for higher precision;
- 3) Carry out a single full temperature range DSC test and some single-stop m-TME II DSC tests to establish the relationship between T_G and T_t (as shown in Figure 3.13);

- 4) Pre-heat a small piece of free-standing SMA sample (the sensor) to above its A_f and then cool it to below its M_f ;
- 5) Maintain the sensor below A_s , and put it together with the item for temperature monitoring;
- 6) At the end of temperature monitoring process, at below A_s , take the sensor out for DSC test (heating from below A_s to well above A_f);
- 7) Compare the resultant DSC curve with that of the full temperature range test (obtained in Step 3);
- 8) If there is not much difference, over-heating should not have happened (i.e., the temperature was always below A_s); if the resultant DSC curve is virtually a straight line, the maximum temperature was over A_f ; if non-straight line type of difference is observed, $T_h \in [T_t - T_G, T_t]$.

Figure 3.14 Illustration of temperature sensor application. (a) To obtain DSC baseline of SMA; (b) to attach temperature sensor to target for monitoring; (c) to run DSC test again and compare.

For tested $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon, it is able to monitor over-heating temperature within $[48^\circ\text{C}, 63^\circ\text{C}]$ with an accuracy of about $\pm 0.5^\circ\text{C}$.

As the nature of m-TME II is to record the volume fraction of transformed martensite, instead of DSC test as applied here, electric resistance test [202] might be an alternative, but its accuracy needs to be carefully examined.

3.3 Further investigation on temperature interruption

So far, c-TME, m-TME I and m-TME II have been systematically investigated. In this section, we present a full picture for the influence of all kinds of temperature interruption on NiTi SMAs.

3.3.1 NiTi shape memory alloys without R-phase

For NiTi SMAs without R-phase, there is only one peak during cooling (A-M) and one trough during heating (M-A) in the full temperature range DSC curve. In most research works on c-TME reported in the literature, such a type of NiTi SMA was used for simplification. In addition to interruption upon the reverse martensitic transformation, i.e., in the heating process, interruption may be applied upon the forward martensitic transformation (in the cooling process) as well.

The same $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon was used to conduct a series of DSC tests. Figure 3.15 shows typical DSC curves in which interruption was applied during the forward martensitic transformation. As shown in Figure 3.15(a), when $M_f < T_c < M_s$ and $T_s < A_s$, in the following cooling process, A-M transformation starts at almost the same temperature where the previous interruption occurs. This is similar to m-TME II, but in the cooling procedure. This phenomenon may be utilized as temperature sensors to detect the overcooling temperature. If $T_s > A_f$, as shown in Figure 3.15(b), the influence of the previous interruption during cooling is removed.

Figure 3.15 Typical DSC curves for interruption during cooling. (a) $M_f < T_c < M_s$, $T_s < A_s$; (b) $M_f < T_c < M_s$, $T_s > A_f$;

We can also combine interruptions during heating and cooling together. Such a type is actually m-TME I discussed in Section 3.2.2.

3.3.2 NiTi shape memory alloys with R-phase

If the same $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon is annealed for half an hour at 500°C , instead of 800°C as in Section 3.1.1, R-phase merges upon thermal cycling (Figure 3.16), due to the influence of annealing conditions [129, 130]. The correspond transformation temperatures associated with austenite to R-phase (A-R) transformation or R-phase to austenite (R-A) transition are R_s , R_f , AR_s , and AR_f , respectively, as marked in Figure 3.16.

Figure 3.16 DSC curve of $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon with R-phase. Solid black line: full thermal cycle; dashed grey line: thermal cycling between R-phase and austenite.

According to Figure 3.16, for this particular material, the R-A and M-A transformations occur within different temperature ranges, although it is possible that these two transitions are within the same temperature range [67]. Normally, the hysteresis for transitions between R-phase and austenite is small.

Figure 3.17 presents the DSC results (some are partially, i.e., only the final heating curve) of three different thermal cycling processes, namely,

- Figure 3.17(a): $100^{\circ}\text{C} \rightarrow T_c=30^{\circ}\text{C} \rightarrow 100^{\circ}\text{C}$;
- Figure 3.17(b): $100^{\circ}\text{C} \rightarrow T_c=30^{\circ}\text{C} \rightarrow T_s=46.5^{\circ}\text{C} \rightarrow T_c=30^{\circ}\text{C} \rightarrow 100^{\circ}\text{C}$;
- Figure 3.17(c): $100^{\circ}\text{C} \rightarrow T_c=30^{\circ}\text{C} \rightarrow T_s=46.5^{\circ}\text{C} \rightarrow T_c=43^{\circ}\text{C} \rightarrow 100^{\circ}\text{C}$;

Since the transformation is only between R-phase and austenite in these tests, essentially they are similar to c-TME or m-TME I. Figure 3.17(b) and (c) reveal that no matter where T_c is, the trough for the R-A transformation in the final heating process does not change very much, in terms of either the curve pattern or AR_s and AR_f . It should be pointed out that by applying a lower heating rate, e.g., $1^{\circ}\text{C}/\text{min}$, in DSC test, c-TME may be observed, but in a very weak form [203, 204]. On the other hand, m-TME II is difficult to achieve due to small hysteresis.

Figure 3.17 DSC curves of full (a) and incomplete R-A transformations (b and c).

Figure 3.18 presents the DSC curves with different T_c s applied during A-R transition (upon cooling). It is apparent that T_c does not virtually change the shape of the trough in final heating.

Figure 3.18 DSC curves of incomplete A-R transformation.

If we further lower T_c to between M_f and M_s , two troughs for the R-A and M-A transformations respectively, occur in the final heating process, as shown in Figure 3.19. T_c may be carefully selected to have about same significance in both transitions.

Figure 3.19 Typical DSC result for $M_f < T_c < M_s$.

Figure 3.20 shows an alternative way to obtain two troughs in the final heating process. Following a thermal history of $100^\circ\text{C} \rightarrow 0^\circ\text{C} \rightarrow T_s = 59^\circ\text{C} \rightarrow T_c = 43^\circ\text{C}/30^\circ\text{C}$

$\rightarrow 100^\circ\text{C}$. The two troughs are for R (which is transformed from M2) to A transformation and M1 to A transformation, respectively.

Figure 3.21 is an example of interruption during both heating and cooling, following the procedure of $100^\circ\text{C} \rightarrow 0^\circ\text{C} \rightarrow T_s = 61^\circ\text{C} \rightarrow T_c = 19^\circ\text{C} \rightarrow 100^\circ\text{C}$. The amplitude of individual troughs may be adjusted by altering T_c and/or T_s . For example, higher T_s reduces the amplitude of M1 to A transition, and higher T_c increases the amplitude of R to A transition and reduces that of M2 to A transition.

Figure 3.20 Typical DSC curves of full thermal cycle (for reference) (a), and incomplete cycle with two troughs (final heating process) (b and c).

Figure 3.21 Typical DSC curves of full thermal cycle (for reference) (a), and incomplete cycle with three troughs (final heating process) (b).

A summary of the different types of temperature interruption and the corresponding transitions in the final heating is listed in Table 3.6 and Table 3.7. For simplification, there is only one stop within each phase transformation temperature range. For the case of multiple stops within each transition, similar discussion may be carried out following the same principle.

Table 3.6 Different types of temperature interruptions and corresponding transitions in the final heating process in NiTi SMAs without R-phase.

$T_c \backslash T_s$	$T_s < A_s$	$A_s < T_s < A_f$	$A_f < T_s$
$T_c < M_f$	N/A	c-TME (Figure 3.1c, Figure 3.7, Figure 3.8)	N/A
$M_f < T_c < M_s$	Partial A-M (Figure 3.15a)	m-TME I (Figure 3.10b)	Partial M-A (Figure 3.15b)
$M_s < T_c$	N/A	m-TME II (Figure 3.10c, Figure 3.11, Figure 3.12)	N/A

Table 3.7 Different types of temperature interruptions and corresponding transitions in the final heating process in NiTi SMAs with R-phase.

$T_c \backslash T_s$	$A_s < T_s < A_f$	$A_s < T_s < A_f (*)$	$A_f < T_s$
$M_f < T_c < M_s$	N/A	R-A followed by M2-A and M1-A (Figure 3.21b)	R-A followed by M-A (Figure 3.19)
$M_s < T_c < R_f$	R-A(almost no influence) (Figure 3.17b)	R-A followed by M1-A (Figure 3.20c)	Full R-A (Figure 3.17a)
$R_f < T_c < R_s$	R-A(almost no influence) (Figure 3.17c)	R-A followed by M1-A (Figure 3.20b)	R-A(almost no influence) (Figure 3.18)

*In this column, a pre-cooling to below M_f is required to ensure full martensite at the beginning.

3.4 Summary

In this chapter, the mechanism for the TME in NiTi SMAs is investigated from the energy point of view. It is revealed that the newly formed M2 should nucleate at the interphase of austenite and M1, where the existing elastic energy drives the transition, so that two separate troughs appear upon final heating.

It is proved that m-TME II may be utilized as the mechanism for temperature sensors to monitor over-heating event. An accuracy of $\pm 0.5^\circ\text{C}$ is achievable for the highest over-heating temperature.

A complete picture for the influence of temperature interruption in NiTi SMAs with/without R-phase is summarized.

Chapter 4 Triple-Shape Memory Effect in NiTi Shape Memory Alloys

Traditionally, only the deformed (temporary) shape and permanent shape are involved in the shape memory effect (SME). Consequently, the conventional SME, may be named as the dual-SME. In recent years, a new phenomenon, namely the multiple-shape memory effect (multi-SME), has been observed in shape memory polymers (SMPs) [118, 120, 126, 128], in which after programming, shape recovery is through one or more intermediate shape(s). If there is only one intermediate shape, it may be named as the triple-shape memory effect (triple-SME).

Due to a totally different working mechanism for the SME, shape memory alloys (SMAs) are not traditionally considered to be able to recover their original shapes in a step by step manner, unless for instance, a gradient transition temperature field is introduced by means of local heat treatment [131], deforming locally into different pre-strains [132], and utilizing a special physical mechanism, e.g., buckling phenomenon in a bilayer composite beam [133].

In this chapter, we demonstrate that by uniformly deforming a piece of NiTi SMA following a specific procedure, the triple-SME can be achieved. Most results and discussions presented in this chapter have been published in [205, 206].

Samples were pre-programmed and then heated for recovery following two different procedures. Differential scanning calorimetry (DSC), uniaxial tension and X-ray Diffraction (XRD) tests were conducted to provide evidence to reveal the underlying mechanism of triple-SME, and thus to optimize the performance.

4.1 Materials and experimental

Two types of NiTi SMA samples were tested. One is $\text{Ni}_{55.8}\text{Ti}_{44.2}$ ribbon, with a cross-section of $2 \times 0.2 \text{ mm}^2$, provided by Mide Technology Corporation (USA). The other is 0.5 mm diameter $\text{Ni}_{55.3}\text{Ti}_{44.7}$ wire from SMA-Inc (USA). After being heat treated at 500°C for one hour, straight ribbons and wires were obtained. Excellent SME was observed in all of them. All tested samples were programmed inside a temperature controllable water tank, in which the temperature can be gradually changed at a constant heating rate of $4^\circ\text{C}/\text{min}$ or cooling rate of $2^\circ\text{C}/\text{min}$.

In each test before programming, pre-heating to 100°C for five minutes was applied to remove any possible residual stress. Unless otherwise stated, room temperature was 25°C . Detailed programming steps for ribbon samples following two different programming procedures, namely small strain procedure (SSP) and large strain procedure (LSP), are as following.

Small strain procedure (SSP) (Figure 4.1)

- (α_1) Cool a piece of straight ribbon sample (cut into a length of 85 mm) from 100°C to 55°C gradually;
- (α_2) At 55°C , bend the sample homogenously to form a curve with a constant radius of 100 mm and hold this shape;
- (α_{3-}) Upon further cooling to room temperature, remove the constraint;
- (α_{3+}) Bend the sample toward the opposite direction with a radius of about 300 mm and hold it;
- (α_4) Further cool the sample to 17°C and hold for 10 minutes before the constraint is removed, wait until temperature is back to room temperature.

Shape recovery test was conducted inside the same water tank, which was gradually heated from room temperature to over 70°C (from β_1 to β_3). Note that one end of the programmed sample was fixed. A camera was used to record the motion of the sample, and a thermocouple was used to monitor the water temperature. Figure 4.1 schematically illustrates the programming and recovery steps. Differential scanning calorimeter (DSC) result in a thermal cycle from 80°C to 17°C and back to 80°C at a heating/cooling rate of 10°C is also included here for reference. Vertical axis is heat flow in arbitrary unit.

Figure 4.1 Illustration of programming procedure of SSP during cooling (from α_1 to α_4) and subsequent shape recovery upon heating (from β_1 to β_3).

Large strain procedure (LSP) (Figure 4.2)

- (A₁) Cool a piece of straight ribbon sample (cut into a length of 85 mm) from 100°C to room temperature gradually;
- (A₂) Wind the ribbon around a cylinder with a diameter of 9 mm for 360° and hold it for one minute;
- (A₃-) At room temperature, release the ribbon sample;

(A_{3+}) Still at room temperature, wind the ribbon sample into the opposite direction around another cylinder with a diameter of 30 mm and hold the shape for one minute;

(A_4) A final shape of nearly straight line is obtained.

The heating procedure for shape recovery was the same as that in SSP.

Figure 4.2 Illustration of programming procedure of LSP.

Surface strain is used hereinafter to evaluate the degree of deformation in each sample during programming and recovery. In both procedures, since the samples are subject to homogenous bending, the corresponding surface strain, which is the maximum, can be estimated based on the thickness of the ribbons and radius of curves, provided that its thermo-mechanical behaviors in tension and compression are symmetric. Hence, we only consider the (initial) positive surface strain hereinafter. We may name the maximum strain involved in the first bending (steps a_2 and A_2) as the programming strain (ϵ_p) and the second bending (steps a_{3+} and A_{3+}) as the auxiliary strain (ϵ_a). As such, the programming strains following above mentioned steps, which are at the top and bottom surfaces of a programmed ribbon, are about 0.1% for SSP and 2.2% for LSP, respectively. Note that by choosing different sized cylinders/curvatures,

different maximum strains can be achieved. The first inward bending direction is defined as the positive direction, thus a negative sign stands for bending toward the other side.

Above mentioned programming procedures are also applicable to NiTi wires. In addition to bending, torsion is another possible mode for programming of NiTi wires. As illustrated in Figure 4.3, one end of a piece of straight 0.5 mm diameter NiTi wire (cut into a length of 100 mm), which was pre-cooled from high temperature to room temperature, was securely anchored to Block B with a free length of 90 mm. Subsequently, it was twisted by $3 \times 360^\circ$ at its free-end counter-clockwise and then by $3 \times 360^\circ$ clockwise.

Figure 4.3 Setup for triple-SME in a NiTi wire in torsion mode.

In the recovery test, the whole setup was heated uniformly inside a hot water bath. A camera that was placed perpendicularly to Block A was used to record the recovery motion in terms of the rotation of a needle fixed to the free-end of the wire.

A few conventional tests were conducted for materials characterization. To name a few, all DSC tests on NiTi samples were carried out using a TA Instruments DSC Q200 at a heating/cooling rate of $10^\circ\text{C}/\text{min}$; uniaxial tensile tests were performed using an Instron 5565 universal testing machine at room temperature; XRD tests were

conducted on NiTi samples using a Philips PW 1830 at a scanning speed of 0.02 %s at room temperature.

4.2 Experimental results and analysis

4.2.1 Experiments results

Snapshots of the recovery sequence in programmed NiTi ribbons after SSP and LSP are presented in Figure 4.4. Relative tip displacement is used to evaluate the motion of the ribbons after SSP, in which the involved deflection is tiny. However, for the ribbons after LSP, rotation angle determined by two tangent lines is used since the deformation is large. For easy visualization and comparison, Figure 4.5(b) shows the relative tip displacement/rotation angle of the ribbon against temperature not only during the whole heating process, but also in the following cooling process (back to room temperature). We can clearly see that the tip moves downward and then upward upon gradually heating from 25°C to 70°C in the case of SSP, while for the case of LSP, it moves in the opposite way, i.e., upward first followed by downward, although in both SSP and LSP, the ribbons were bent twice in the same way (upward first and then downward).

Figure 4.4 Snapshots of recovery sequence in NiTi ribbons after being programmed following SSP (a₁-a₄) and LSP (b₁-b₆).

Figure 4.5 Triple-SME in NiTi ribbon. (a) DSC result of strain/stress-free sample upon heating (refer to Figure 4.1); (b) relative tip displacement/rotation angle θ against temperature curves.

Since we can always see a motion reversal event upon monotonic heating in both SSP and LSP, which forms an apparent intermediate shape/position between the temporary shape and the original shape, this is the triple-SME.

In the subsequent cooling process (from 70°C to 25°C), there is not any visible motion at all in all ribbons, which excludes the possibility that the ribbons have been developed with the so called two-way SME, i.e., the ability to switch between two shapes (high temperature austenite shape and low temperature martensite shape) in thermal cycling [3, 5]. It is confirmed that high temperature austenite shape is the only shape that these ribbons can memorize [3].

Figure 4.6 presents the snapshots of typical two-step recovery in a 0.5 mm diameter NiTi wire which was programmed by slightly bending (following LSP). It is clear that the triple-SME has been produced successfully. In addition, Figure 4.7 shows the snapshots of the recovery sequence in a 0.5 mm diameter NiTi wire after being programmed in torsion mode. The exact rotation angle is indicated by a needle fixed to the free-end of the wire. As we can see, the needle rotates almost one full cycle counter-clockwise before clockwise back to the original position.

Figure 4.6 Snapshots of recovery in a pre-bent NiTi wire (two parallel pieces) after LSP with 0.8% ϵ_p .

Figure 4.7 Snapshots of recovery in a pre-twisted NiTi wire after LSP with 2.7% ϵ_p .

Above experiments demonstrate that even without introducing a gradient transition temperature field, the triple-SME is achievable in a range of NiTi SMAs, and is applicable to different motion modes. However, in order to realize the triple-SME, there are certain conditions on the material itself and certain requirements on the programming procedure.

4.2.2 Further experimental investigation

As shown in Figure 4.5(b), it seems that the temperature ranges for the two-step shape recovery match well with the temperature ranges of the two-step transition in DSC result in Figure 4.5(a). A series of DSC tests were conducted on the NiTi ribbon and the results are presented in Figure 4.8. All tests were started from high temperature austenite phase and cooling was stopped at some different temperatures (T_c). We can see up to three distinct phases, namely austenite (A), martensite (M) and R-phase (R). Depending on the exact cooling stop temperature T_c , the DSC curve in the subsequent heating process may follow different patterns (similar DSC results have been reported previously [207]). If T_c is between the martensite start temperature (M_s) and

martensite finish temperature (M_f), a mixture of martensite and R-phase is resulted at the end of the cooling process. We identify the first transition upon subsequent heating as R to A transition and the second one as M to A transition, provided that pure martensite is able to transform into austenite directly. However, it is still possible that the transition is via R-phase. In order to have two apparent transitions, not only the temperature ranges for the R to A transition and for the M to A transition must be well separated, but also both transitions should be significant enough. The first requirement is the condition for the triple-SME in SMAs, while the second requirement is for the programming procedure.

Figure 4.8 Series of DSC results of NiTi ribbon with different T_c s.

It should be pointed out that R-phase can only be observed in some Ni-rich NiTi SMAs [69]. Apparently, the triple-SME cannot be achieved in those NiTi SMAs

without R-phase. Even in NiTi SMAs with R-phase, if the temperature range for the R to A transition is too close to that of the M to A transition, as shown in Figure 4.9(a), the triple-SME is also not applicable. A peak to peak temperature gap of over 10°C between the R to A transition and the M to A transition might be sufficient. Figure 4.9(b) is the DSC result of the above tested NiTi wire, in which the gap is over 10°C. Above tested NiTi ribbon has a gap of over 10°C (Figure 4.8). The second requirement is what we should bear in mind in selecting the right programming parameters to ensure a balance in terms of significance in both transitions. Although the transition from M to A upon heating might be directly, or indirectly (via R-phase), for both cases, the triple-SME is achievable.

Figure 4.9 Typical DSC results of two NiTi SMAs with different transition temperature gaps. (a) 5°C gap (sample bought from Image SI Inc, USA, cooling stopped at -10°C; R_f is the finish temperature of A to R transformation); (b) 11°C gap (NiTi wire, cooling stopped at 8°C).

Uniaxial tensile tests were conducted on these NiTi ribbons with two different initial phases, i.e., martensite and R-phase, and to two different strains, namely 0.1% and 0.8%, respectively. The applied strain rate in both loading and unloading is 10^{-5} /s (to a maximum strain of 0.1%) or 10^{-4} /s (to 0.8%), respectively. As revealed in Figure 4.10, after unloading from a maximum tensile strain of 0.1%, the residual strain is always small, which indicates that the deformation is largely elastic in both phases. On the

other hand, after being stretched to 0.8%, the residual strain becomes significant, in particular in the R-phase sample, partially due to that the required tensile stress for 0.8% strain in the martensite sample is much higher than that of the R-phase sample. The residual strain in the martensite sample is resulted from the stress-induced detwinning, i.e., reorientation of martensite variants [3]; while for the R-phase sample, as confirmed by the result of XRD test shown in Figure 4.11, remarkable residual strain should be the result of the growth of martensite at the expense of R-phase, which is consistent with what is mentioned in [208] that over 0.5% tensile strain may result in the transition of R-phase into detwinned martensite (DM). Therefore, it is clear that the martensite produced by SSP is thermally induced, while for LSP, stress-induced martensite is dominant.

Figure 4.10 Stress vs. strain curves of NiTi ribbon in martensite (pre-cooled in iced water) and R-phase (cooled from high temperature austenite to room temperature).

Figure 4.11 XRD results of NiTi ribbons after different treatments. (a) $M_s < T_c < R_f$, without stressing; (b) $T_c < M_f$, without stressing; (c) after SSP; (d) after LSP.

4.2.3 Mechanisms and conditions

Based on above experimental results, the underlying key mechanisms and conditions for the triple-SME in NiTi SMAs can be worked out as following.

For simplicity, we assume that at a given temperature, the thermo-mechanical behaviors of a SMA ribbon in both tension and compression are about the same. Consequently, when the SMA ribbon is in bending, we only need to investigate half side of the ribbon, either in the tension side or in the compression side as shown in Figure 4.12 and Figure 4.13, which schematically illustrate the mechanisms for SSP and LSP, respectively. Bold line represents the strain distribution in the section at one side (either tension or compression). Labels correspond to the programming steps in

Figure 4.1. Black dot in β_1 – β_3 essentially represents the macroscopic tip motion of the ribbon. A, R and M denote austenite, R-phase and martensite, respectively.

Figure 4.12 Schematic illustration of the mechanism for the triple-SME after SSP.

Recall Figure 4.1 for the programming procedure of SSP. When being bent slightly at high temperatures (α_2), the ribbon is austenite and deforms only elastically. However, upon holding this shape and cooling the ribbon for full A to R transformation (α_3^-), all austenite becomes R-phase. The resultant R-phase has a special orientation in favor of the applied stress to minimize the internal stress. In the next step (α_3^+), the ribbon is bent slightly into the opposite direction, so that the deformation is largely elastic. R to M transformation starts only when temperature is below M_s (α_4), which is initialized from the high stress/strain region, namely the top surface in Figure 4.12. Note that T_c should be carefully chosen to ensure a good balance between martensite and R-phase. This is essential to ensure two remarkable transitions in the subsequent heating for a remarkable triple-SME. Since the residual strain after being strained to 0.1% is small, the remaining R is largely able to elastically recover after unloading, which indicates

that the orientation of R (shearing toward right) is largely maintained; while the martensite has an opposite orientation (shearing toward left).

Now there are two phases in the ribbon, R-phase and martensite, but with opposite shearing directions. Upon heating, R-phase transforms into austenite first and then martensite recovers its original austenite shape at a higher temperature range. Correspondingly, the first shape recovery causes the black dot (β_1) to move to the left (β_2). Upon further heating the dot moves to the right (β_3). Virtually a forward and then backward motion is produced upon heating. This is the mechanism for the triple-SME after SSP. By carefully selecting the curvature in bending, we are able to see that upon gradually heating a straight beam moves downward and then upward, before it becomes straight again. Above discussion is based on some simplifications in order to reveal only the key issues. In reality, different phases may not distribute so evenly as distinct layers, but tangle with each other, in particular at the inter-phase region. However, these issues should not affect the fundamentals behind the triple-SME after SSP.

Before we start to discuss the underlying mechanism for the triple-SME after LSP, two important points should be noted here. Programming in LSP is all performed at room temperature, which is between R_f and M_s of a NiTi SMA; while that in SSP is during gradually cooling and T_c is a key programming parameter. In addition, the maximum strain in LSP must be over 0.5%; while in SSP the maximum strain should be much lower, as around 0.1%.

Figure 4.13 Schematic illustration of the mechanism for the triple-SME following LSP.

Refer to Figure 4.13 and recall Figure 4.2. At room temperature, the ribbon is initially in R-phase (A_1) after cooling from high temperature austenite phase. Large deformation in terms of bending causes stress-induced R to M transformation at the top part (as confirmed by XRD test in Figure 4.11). Less strained part undergoes reorientation and becomes R_1 ; while in the center part (R), it is elastic deformation (A_2). As such, after unloading, R is able to elastically recover its original shape, while the other two parts largely maintain the deformed shape (A_{3-}). Second bending toward the opposite direction also induces martensite reorientation but only partially (at top surface, where the strain is maximum), namely M_1 , and in almost all R_1 (A_{3+}). Since the strain is not over 0.5%, it becomes R_2 , shearing toward right. Again, in the center part, R is only elastically deformed. After elastic recovery upon full unloading, all phases are more or less well maintained as illustrated in (A_4). Subsequently, upon heating, the recovery process starts and consists of two steps: the R to A transformation happens first, which causes the dot to move to the right (B_2), followed by the M to A transformation, which results in the dot moves back (B_3). Hence, macroscopically, we see the motion is upward and then downward as illustrated in

Figure 4.4(b₁-b₆). In this particular case presented in Figure 4.4, the ribbon was programmed after LSP and changed its shape from straight to curve and then back to straight. The associated maximum strain variation in the triple-SME of the tested ribbon is about 0.35%.

It should be pointed out that the triple-SME programmed by either SSP or LSP is fully repeatable, without any noticeable change in the thermo-mechanical properties in all the tested samples. The triple-SME may not be limited to some particular NiTi SMAs but rather is a generic feature of a range of SMAs as long as the conditions on material itself and programming procedure are satisfied.

4.3 Further discussion

Obviously, the triple-SME reported here enables higher flexibility in design, and thus adds in a new dimension for SMA applications. With one intermediate shape during shape recovery, a piece of SMA can be programmed for more sophisticated motion generation that is not achievable in traditional dual-SME. Since the triple-SME is a one-time phenomenon, the same piece of material can be re-used without worrying any permanent change in material properties.

4.3.1 Flexibility in programming and recovery

Figure 4.14 shows that a SMA coil made of the same NiTi ribbon as used above shrinks and then expands upon gradual heating. This is achieved by contracting the coil first and then expanding it during programming following LSP. Such a shape switching feature may be utilized as a retractable mechanical coupling. If we reverse the deformation direction during programming, expansion followed by shrinkage in the same piece of NiTi SMA coil is achieved (Figure 4.15), which may be utilized as

a retractable medical stent. Above cases demonstrate the flexibility to achieve programmed motions, so that “The material is the machine” [113].

Figure 4.14 Shrinkage followed by expansion of a NiTi SMA coil upon monotonic and gradual heating.

Figure 4.15 Expansion followed by shrinkage of a NiTi SMA coil upon monotonic and gradual heating.

A piece of SMA wire ($\text{Ni}_{55.3}\text{Ti}_{44.7}$, 0.18 mm diameter) was used to further demonstrate the flexibility in programming and recovery. The wire was wound around a cylinder with a diameter of 2 mm (Figure 4.16) or 10 mm (Figure 4.17), followed by annealing at 500°C for 30 minutes with shape fixed. After the annealing, a NiTi SMA spring was obtained. Depending on the actual manner in LSP, elongation–contraction (axial direction) or expansion–contraction (radial direction) of this spring has been realized, as shown in Figure 4.16 and Figure 4.17, respectively.

Figure 4.16 Elongation followed by contraction in a 2 mm diameter NiTi spring upon monotonic and gradual heating.

Figure 4.17 Expansion followed by contraction in a 10 mm diameter NiTi spring upon monotonic and gradual heating. White dashed line indicates the original diameter of the spring.

It should be pointed out that traditional SMA devices are lack of the retraction function since they are mostly based on the dual-SME [23, 209, 210]. Although the material two-way SME may be utilized for the retraction function, as revealed in Figure 4.18, the intrinsic problem of low reliability and low recoverable strain in the two-way SME has limited its applications.

Figure 4.18 NiTi SMA stent based on material two-way SME [55].

4.3.2 Recovery force

Constrained recovery test was conducted using the same NiTi ribbon coil as shown in Figure 4.15. After being programmed following LSP, the coil was placed inside the temperature controllable chamber of Instron Universal Tester 8848 as illustrated in Figure 4.19 (inset). The coil was heated to over 70°C at a rate of 1°C/min with its expansion constrained. The evolution measured of force is plotted in Figure 4.19, together with the evolution of diameter measured in a free recovery test. It is obvious that the general trend in both force and diameter against temperature follows the same pattern. A maximum force of 52 mN is recorded for this particular configuration, and the change in diameter is from 36 mm to 45 mm and then back to 33 mm.

Figure 4.19 Evolution of recovery force and diameter in NiTi SMA coil during heating. Inset: schematic illustration of the setup for constrained recovery test.

4.3.3 Recovery strain

As mentioned in Section 4.2.3, in the case of SSP, since martensite is generated during cooling, the volume fraction of martensite after programming is mainly determined by T_c in step a_4 (Figure 4.12). On the other hand, in the case of LSP (Figure 4.13), martensite is stress-induced, and its volume fraction is highly dependent on ϵ_p and ϵ_a .

A series of tests were conducted on NiTi ribbons following a similar procedure as in Figure 4.1 and Figure 4.2 with different programming parameters. Figure 4.20 reveals the evolution of surface strain during shape recovery with three different T_c s, and a constant ϵ_p of 0.1% in SSP, and with three different ϵ_{as} , and a constant ϵ_p of 0.8% in LSP. These were achieved by controlling the cooling temperature and choosing cylinders of different size in bending. Since all curves follow the similar trend as in Figure 4.5, only the start, turning and finish points, i.e., when recovery start, direction switch and recovery finish, are plotted for comparison.

Figure 4.20 Two-step recovery with constant ϵ_p and different T_c s (from top to bottom: 19°C, 17°C and 13°C) or ϵ_{as} (from bottom to top: 0.80%, 0.83% and 1.18%).

Obviously, for SSP, with the decrease of T_c , more forward R-M transformation completes, which results in a higher volume fraction of martensite after programming. Consequently, surface strain at the start point is smaller and even becomes negative. Strain at the turning point follows the same trend. For LSP, ϵ_a plays a similar role as that of T_c in SSP. The function of T_c and ϵ_a is actually to determine the relative ratio of martensite and R-phase in a programmed material, and thus how much strain is recovered in each step of shape recovery. We may conclude that the triple-SME can be conveniently optimized by means of tailoring these parameters.

From engineering point of view, LSP is more of practical interest than SSP since a far larger strain is involved and programming is easier. As demonstrated in Figure 4.5, by carefully choosing ϵ_a in programming, it is possible to have a zero surface strain after programming. As such, virtually we can see that a piece of straight NiTi ribbon bends upward significantly and then downward to become straight again upon gradual heating. We may name the strain at the turning point as the reversible strain (ϵ_r), and utilize it as a parameter to quantitatively evaluate the significance of the triple-SME.

A series of tests were conducted following the same procedure as introduced in Figure 4.2. Different ϵ_p s and ϵ_a s were selected so that surface strain of the programmed samples were about zero, and hence shape recovery in them followed the same pattern as that shown in Figure 4.5(b) (LSP). A typical relationship between ϵ_r and ϵ_p is presented in Figure 4.21. It is noticed that ϵ_r increases with the increase of ϵ_p only at small ϵ_p , since more elastic energy is stored inside the material during distortion. However, ϵ_r decreases upon further increase of ϵ_p . This is due to that nearly all R-phase transforms into martensite when a larger strain is applied, thus only a smaller amount of R-phase is left for the reverse transformation into austenite, which results in a smaller recovery strain. Therefore, we may conclude that in order to have apparent triple-SME (LSP), ϵ_p should be between 2% and 4% for this particular NiTi SMA.

Figure 4.21 Typical relationship between ϵ_r and ϵ_p in the triple-SME.

As for programming in torsion mode (refer to Figure 4.7), the corresponding ϵ_p and ϵ_r can be calculated based on length and diameter of the sample, and total rotation angle [67]. In above mentioned particular case (Figure 4.7, twisted $3 \times 360^\circ$ counter-clockwise and then $3 \times 360^\circ$ clockwise), ϵ_p is about 2.72% and ϵ_r is about 0.87%. As compared with that in bending, it appears that torsion is more efficient than bending for the triple-SME. However, in another test in which we twisted the wire forward and then backward by four turns (in which the corresponding ϵ_p is about 3.63%), ϵ_r decreases sharply to 0.12%. It confirms the need to optimize the programming parameters in order to achieve the best performance for the triple-SME.

4.3.4 Recovery temperature

Based on the testing results reported in Figure 4.21, Figure 4.22 reveals the influence of ϵ_p on the temperatures at the start, turning and finish points. It appears that all these temperatures rise with the increase of ϵ_p , and the transition temperature range becomes narrower, which indicates the influence of pre-strain on SMA [132]. According to this finding, without altering the material properties of a SMA at all, we may tailor the temperature range of the triple-SME to meet the exact requirement.

Figure 4.22 Variation of transition temperature as a function of ϵ_p .

4.3.5 Heating method

Apart from monotonic and gradual heating, two-step heating may also be applied for two-step shape recovery, i.e., heating to the turning point in the first heating process, and heating to above finish point in the second heating process. This should be more practical than gradual heating, as intermediate shape may be required to last a long period of time (or even forever).

Similar tests as reported in Figure 4.16 and Figure 4.17 were repeated in the temperature controllable water bath, but heating was conducted two times. Snapshots are presented in Figure 4.23 and Figure 4.24, respectively. It should be pointed that no visible shape change was observed when both sample were cooled back to room temperature. Shape change only occurred when temperature was higher than the previous heating temperature. As such, the ability to keep the intermediate shape in the triple-SME, is confirmed.

Figure 4.23 Elongation/contraction in a NiTi spring upon heating in water with different temperatures. (a) 25°C, original length: 10 mm; (b) 25°C, stretched to 75 mm; (c) 25°C, compressed back to 15 mm; (d) in 50°C water, length stabilized at 24 mm; (e) in 80°C water, length stabilized at 10 mm (fully recovered).

Figure 4.24 Expansion/contraction in a NiTi spring upon heating with different temperatures. (a) 25°C, original diameter: 10.9 mm; (b) 25°C, enlarged to 19 mm; (c) 25°C, twisted back to 11.6 mm; (d) in 50°C water, diameter stabilized at 12.7 mm; (e) in 80°C water, diameter stabilized at 10.9 mm (fully recovered).

4.4 Summary

We have proposed two approaches, namely SSP and LSP, to realize the triple-SME in NiTi SMAs. The requirements on the material selection and programming parameters for the triple-SME are identified. The underlying mechanisms are revealed, which are

supported by additional experiments. The influence of key parameters in programming is investigated.

Essentially, the triple-SME should not be a unique phenomenon only limited to some particular types of SMAs. It should be achievable in a range of SMAs, as long as the transition is in a multi-stage manner, and the requirements identified here are satisfied. This effect may be utilized for novel devices, such as retractable stent.

Chapter 5 Shape Memory Effect in Nail Keratin

While the shape memory effect (SME) has been observed in many conventional or specially synthesized polymers [7, 8, 10], relative less research works have been reported on biological polymers. In this chapter, we explore the SME in human nail, in which keratin protein is the main component.

In the course of this study, human nail was used. Standard thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed to characterize its thermal properties. Subsequently, a series of shape recovery tests were carried out to investigate the effects of two stimuli, namely, heat and water. The results in bending and indentation were compared. The feasibility to achieve triple-SME utilizing both heat and water as stimuli was demonstrated.

5.1 Introduction of keratin protein

Protein is a kind of biological polymer of polypeptide chains that plays vital roles in all living things. As believed, there are at least three basic levels of structure in proteins, namely: primary, secondary and tertiary/quaternary [211]. The primary structure is a linear sequence of amino acids along the polypeptide chain. The secondary structure refers to the local conformation of amino acid residues. The tertiary structure represents a three dimensionally folded polypeptide chain, when the elements of the secondary structure interact and fold into a compact globular structure. These interactions include non-covalent bonds, such as electrostatic interaction, van der Waals interaction, hydrophobic contact and hydrogen bond between non-backbone groups, as well as covalent bond such as disulfide bridges [212].

Denaturation is a process in which proteins lose their tertiary and secondary structure at the presence of chemical, radiation or heat, etc. [213]. The change of physical status in egg white from liquid to solid upon heating is one of the typical examples of protein denaturation. Different types of proteins may have different denaturation temperatures. In most cases, protein denaturation is irreversible [214], and is accompanied with a significant change in material properties.

Keratin is a family of fibrous structural proteins. It is the key structural component of hair and nails [215]. Keratin monomers assemble into bundles to form intermediate filaments, which are tough and insoluble, and form strong unmineralized tissues found in reptiles, birds, amphibians and mammals [216].

Nails of mammals contain α -keratin. As reported in literature [217, 218], the structure of nail is similar to that of hair. However, the orientation of intermediate filaments of human nail is perpendicular to the growth axis of nail [219], while that of hair is parallel to the matrix [159].

5.2 Materials and experimental

Human nails excised from an Asian male adult were used in the course of this study. The materials were kept in room temperature (22~25°C) air (relative humidity 60~70%) for more than one week before any treatment and tests were conducted.

5.2.1 Thermal characterizations

Two types of standard thermal analysis tests, namely thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), were conducted. Unless otherwise stated, all TGA tests in this chapter were conducted using TGA 2950 (TA Instrument, US) at a heating rate of 10°C/min, under nitrogen atmosphere with a

sample size of 10~20 mg; all DSC tests in this chapter were conducted using DSC Q200 (TA Instrument, US) at a heating and cooling rate of 10°C/min, under nitrogen atmosphere with a sample size of 10~20 mg.

Figure 5.1 shows the TGA result of as prepared nail upon heating from room temperature to 900°C. The weight loss till around 200°C should be the result of the evaporation of moisture. Upon further heating up to 400°C, a higher rate of weight loss indicates that the sample is largely decomposed. As such, the maximum temperature for DSC test was limited to below 200°C, to ensure that no material decomposition happens at the testing temperature range of DSC test. On the other hand, as shown in the later discussion, we can find that water content heavily influences the thermo-mechanical behaviors of nail, thus water content of nail should be determined before any other tests.

Figure 5.2 reveals the DSC results of as prepared nail. In the first thermal cycle, T_g is around 72°C, which is determined as the median point of the onset and offset points as illustrated. Upon further heating, a wide trough occurs between 100°C and 160°C. According to literature [158, 220], this trough corresponds to the denaturation of protein. In the second thermal cycle, the heating curve is almost a straight line, which confirms that the denaturation of nail keratin is irreversible [221-223]. As such, in the following study, heating was limited to below 100°C to eliminate the influence of protein denaturation. Unless otherwise stated, Furnace (Elite BRF14/5) was used to heat samples to a specific temperature for five minutes. The relative humidity inside the furnace was about 50%.

Figure 5.1 TGA result of as prepared nail.

Figure 5.2 DSC result of as prepared nail.

5.2.2 Physical characterizations

Although human nail normally has an irregular shape, we may roughly treat it as a homogeneous curved beam with an even thickness throughout the whole sample. For simplicity, we assume that the thermo-mechanical behaviors of a nail in both tension and compression are about the same. Hence the neutral layer, i.e., the layer which does not change its length in bending, is at the center of the curved beam.

Figure 5.3 illustrates the geometry of a curved beam upon bending. Dashed line presents the neutral layer, d is the beam thickness, r and θ represent the radius and angle of the neutral layer, subscript i ($i=1\sim4$) stands for the different stage in

programming and recovery. We may assume that the original nail as shown in Figure 5.3(a) is strain/stress free, so that Figure 5.3(b)~(d) actually correspond to ε_L , ε_U and ε_R , which are defined in Figure 2.4, respectively.

Figure 5.3 Schematic illustration of a curved beam upon bending. (a) Original shape; (b) upon loading; (c) upon unloading; (d) after the recovery.

Therefore, we can get the following geometric relationships,

$$\begin{cases} l_{n1} = l_{n2} = l_{n3} = l_{n4} \\ l_{ni} = r_i \cdot \theta_i \\ l_{oi} = (r_i + d/2) \cdot \theta_i \end{cases} \quad (5.1)$$

where l_n and l_o stand for the length of neutral layer and outer surface, respectively.

The maximum strain due to bending appears at the inner/outer surface. Since we have assumed that the thermo-mechanical behaviors of a nail in both tension and compression are about the same, in the following discussions, we use surface strain to evaluate the extent of deformation.

Upon loading, the maximum programming strain ε_L may be expressed as,

$$\begin{aligned} \varepsilon_L &= (l_{o1} - l_{o2}) / l_{o1} \\ &= [(r_1 + d/2) \cdot \theta_1 - (r_2 + d/2) \cdot \theta_2] / (r_1 + d/2) \cdot \theta_1 \\ &= d \cdot (\theta_1 - \theta_2) / (2l_{n1} + d \cdot \theta_1) \end{aligned} \quad (5.2)$$

Here d , l_{nl} and θ_I vary from sample to sample. For all tested ones, d varies between 0.42 mm and 0.48 mm, and θ_I varies between 101 ° and 119 °. ε_L is a function of θ_2 only. ε_U may be determined by:

$$\varepsilon_U = d \cdot (\theta_1 - \theta_3) / (2l_{nl} + d \cdot \theta_1) \quad (5.3)$$

Furthermore, ε_R , which is the surface strain after shape recovery, may be defined in the same way.

For a particular sample, the shape fix ratio R_f and shape recovery ratio R_r may be calculated as,

$$R_f = \frac{\theta_1 - \theta_3}{\theta_1 - \theta_2} \times 100\% \quad (5.4)$$

$$R_r = (1 - \frac{\theta_1 - \theta_4}{\theta_1 - \theta_3}) \times 100\% \quad (5.5)$$

During programming and recovery, angles of a sample at each stage ($\theta_1 \sim \theta_4$) were measured and recorded. In some tests, samples were placed between two aluminum plates of 3 mm thickness and clamped by two clips (applied force was about 20 N) for one minute to flatten θ_2 to 0 °. Based on above definitions, if a typical nail sample ($d=0.45$ mm, $\theta_I=110$ °, $r_I=9.5$ mm) was flattened ($\theta_2=0$ °), the corresponding programming surface strain ε_L is around 2.3%. For θ_2 other than 0 °, samples were manually wound around aluminum cylinders of different sizes and held for one minute.

5.3 Heating-induced shape memory effect

5.3.1 Deformation by bending

In these tests, nail sample is deformed by means of mechanical bending at room temperature. This programming approach is referred as the “stress-fix” method

hereinafter. The free standing temporary shape can sustain for a long period of time unless a right stimulus is applied. Figure 5.4 shows the shape change process of a stress-fixed nail sample upon heating. To be more convincing, the nail was pre-bent to the other side during programming and the corresponding θ_2 was -90° and ε_L was about 4.2%. Upon heating to 60°C , remarkable shape change is observed within one minute. Unless otherwise stated, the maximum heating temperature for heating-induced SME discussed in this chapter is 80°C .

Figure 5.4 Snapshots of heating-induced shape recovery of nail at 60°C [104].

A series of tests were conducted following the procedure mentioned in Section 5.2.2. For these samples, the programming surface strain ε_L was between 3.2% and 3.5%, such that the residual surface strain ε_U was around 2.2%. To compare shape fixity ratio R_f , all samples were subject to a ε_L of about 2.3%. To compare shape recovery ratio R_r , ε_U of all samples was about 2.2%, which was realized by choosing different ε_L since different programming methods and strain may have different R_f .

Figure 5.5 plots the evolution of shape recovery ratio R_r against heating temperature of three samples. As we can see, the shape virtually remains almost the same at above 60°C . Since the average R_r is only about 32%, the heating-induced SME of nail is not so good when compared with typical SMP, such as polyurethane, in which R_r is usually over 95% [82, 224, 225].

Besides mechanical deformation, the temporary shape of a piece of nail may also be obtained by means of “heating-fix”. The procedure is as following:

- Flatten the sample using two aluminum plates of 3 mm thickness and clamp them with clips, applied force was about 20 N ($\epsilon_L \approx 2.3\%$);
- Put the whole set-up in a furnace for 15 minutes at 60°C and about 50% relative humidity;
- Take out the whole set-up and cool in room temperature air for 30 minutes.

The shape fixity ratio R_f is improved significantly. The average R_f of heating-fix ($\epsilon_L \approx 2.3\%$) is about 93%, as compared with 21% for stress-fix ($\epsilon_L \approx 2.3\%$).

Figure 5.5 R_r of heating-induced shape recovery in stress-fixed nails ($\epsilon_U \approx 2.2\%$).

Figure 5.6 shows the evolution of shape recovery ratio R_r against heating temperature of three nail samples which were heating-fixed at 60°C ($\epsilon_L \approx 2.3\%$ and $\epsilon_U \approx 2.1\%$). It is apparent that R_r is significantly lower than that presented in Figure 5.5, where samples were stress-fixed, and virtually no further shape change is observed after the temperature rises to above 70°C .

Figure 5.6 R_r of heating-induced shape recovery in heating-fixed nails ($\epsilon_U \approx 2.1\%$).

Evolution of surface strain in a cyclic heating-induced SME test of nail is presented in Figure 5.7, together with R_r in each cycle. The programming procedure of each cycle is as following: the sample was first stress-fixed to $\varepsilon_L \approx 3.0\%$, and then heated to 80°C for shape recovery. Above procedure was repeated for five times on the same piece of sample. As we can see in Figure 5.7, the surface strain before heating is always about 1.8% , but the surface strain after heating increases with the increase of cycle number, so that R_r actually decreases gradually. In the first cycle, R_r is about 35% , which agrees with that reported in Figure 5.5. However, R_r in the fifth cycle is reduced to 7% only, which indicates that the heating-induced SME deteriorates rapidly upon cycling.

Figure 5.7 Evolution of surface strain and R_r in cyclic heating-induced SME in stress-fixed nail.

5.3.2 Deformation by indentation

Heating-induced SME at microscopic scale was also studied via indentation test. The nail samples were well pre-polished before indentation. Micro-hardness tester from CSM Instrument, Switzerland was used for indentation atop nail surface. The indenter was sphere-conical diamond with $R=200\ \mu\text{m}$ and $\alpha=90^\circ$. The applied linear loading and unloading rates were $2\ \text{N/min}$, pause time was 10 seconds, maximum load was $5.5\ \text{N}$, and contact force threshold was $0.01\ \text{N}$.

A typical indentation result is presented in Figure 5.8. We can see that the applied normal force increases in an almost linear manner with the increase of penetrate depth, and the residual indentation depth after unloading is about 13 μm .

Figure 5.8 Typical loading/unloading curve of indentation test on nail for heating-induced SME.

Figure 5.9 shows the 3D scanned images of microscopic heating-induced shape recovery process of indented nail, using confocal surface profiler with an objective lens of 50x. Figure 5.10 compares the corresponding cross sections of each stage as in Figure 5.9. It is revealed that the maximum indentation depth is around 12~13 μm , which agrees with that in Figure 5.8. After heating to three different temperatures, namely 40, 60 and 80°C, gradual shape recovery is observed as shown in Figure 5.9(c)~(e). Almost no further shape change is observed upon heating to higher temperatures, so that at microscopic scale, full recovery is also not possible.

Figure 5.9 3D scanned images of heating-induced recovery in nail at microscopic scale. Left: 3D view; right: top view. (a) Original; (b) after indentation; (c) after heating to 40°C; (d) after heating to 60°C; (e) after heating to 80°C.

Figure 5.10 Comparison of cross sections of microscopic heating-induced SME in nail.

Based on the resulted normal force-penetration depth curve of an indentation test, it is possible to calculate the amount of strain based on the formula of von Mises equivalent strain through a numerical simulation [226-231]. Schematic illustration of the geometric parameters of an indentation test is presented in Figure 5.11, in which P is the normal force, R is the radius of indenter, h is the indentation depth, h_c is the contact depth and a_c is the projected contact radius.

Figure 5.11 Schematic illustration of an indentation test using spherical tip.

Correspondingly, the relationship of indentation strain ($\varepsilon_{\text{indentation}}$) and equivalent strain ($\varepsilon_{\text{equivalent}}$) is given by [232],

$$\varepsilon_{\text{indentation}} \approx 0.2 \frac{a_c}{R} \approx \varepsilon_{\text{equivalent}} \quad (5.6)$$

where

$$a_c = \sqrt{2h_c R - h_c^2} \quad (5.7)$$

For an indentation test illustrated in Figure 5.8, h_c may be derived using Oliver and Pharr's method [233], i.e.,

$$h_c = h - \kappa P / S \quad (5.8)$$

where $S=dP/dh$ is the stiffness, which may be experimentally measured from the unloading curve. According to Figure 5.8, $S=1.375$ N/ μm . The geometric coefficient κ for spherical tip is 0.75. Therefore, the equivalent programming strain ε_L in indentation is about 10.61%, and the residual strain ε_U upon unloading is about 7.26%. After heating to 40, 60, and 80°C, the remaining equivalent strains are 6.53%, 5.60% and 4.96%, respectively. As such, R_r is calculated as 31.7%, which is very close to the previous result in macroscopic bending tests, in which the average R_r is about 32%. It implies that the recoverable strain of this nail for heating-induced SME is about 2.3%.

5.4 Water-induced shape memory effect

5.4.1 Deformation by bending

Water content is believed to be one of the most important factors that influence the physical properties of nail [217, 234, 235]. Figure 5.12 reveals the DSC result of wet nail that has been immersed in distilled water for 60 minutes. It is shown that upon heating in the first thermal cycle, the trough which indicates denaturation shifts to a lower temperature range significantly. The result of the second cycle is similar to that of dry nail as shown in Figure 5.2, which clearly indicates the evaporation of water after the first cycle. The results of the third and fourth cycles are about the same and are similar to the second cycle in Figure 5.2 for denatured keratin. A high endothermic heat flow in the first cycle is largely due to water evaporation [236] and it is hard to spot a clear T_g from the curve [237]. Consequently, the T_g is estimated based on the second cycle as around 48°C.

Figure 5.12 DSC result of wet nail.

A piece of nail was bent to $\epsilon_L \approx 4.2\%$ and immersed into room temperature distilled water. Figure 5.13 shows that almost full shape recovery is accomplished within 30 minutes. As such, this is the water-induced SME. Unless otherwise stated, all water-induced SME tests in this chapter were conducted by means of immersing a sample in room temperature distilled water for 60 minutes.

Figure 5.13 Snapshots of water-induced shape recovery in nail.

A few types of pre-treatments were applied to vary the status of nail samples for different water contents. The procedures to prepare them are listed as following,

- Status A: after immersing into room temperature distilled water for 60 minutes;
- Status B: after keeping the sample of status A in room temperature air for 24 hours;

- Status C: after heating the original sample in 80°C air (relative humidity 50%) for 30 minutes;
- Status D: after heating the original sample in 100°C air (relative humidity 50%) for 30 minutes;

Nails of status D are brittle and easily broken even by slight bending. We may consider status D as “complete dry”, and hence water content in a nail may be defined as:

$$\text{Water content} = (w - w_0) / w_0 \times 100\% \quad (5.9)$$

where w is the current weight of a sample and w_0 is the weight of its status D. Therefore, water content of a sample in status D is 0%. The variation of water content of eight samples after different treatments is presented in Figure 5.14.

Figure 5.14 Water content of nail under different treatments.

The average water content of original one (without any treatment), status A, B and C are about 9.2%, 30.0%, 10.0% and 2.8%, respectively. The results agree with the previous reported maximum water content of 30% for human nail [238]. As shown in Figure 5.14, a sample may switch among status A, B and C easily by means of natural drying (place in room temperature air) or forced drying (applying moderate heating) and wetting in water. Such cycling may repeat many times without causing any

notable deterioration in nail. However, irreversible deterioration in thermo-mechanical properties appears when nail is subject to severe heating and becomes status D. Even nail of status D is put into water again, hardly any SME is observed.

Figure 5.15 reveals the evolution of water content in three nail samples against wetting time. As we can see, at room temperature, it takes about 60 minutes for nail to be fully wetted, and the water content rises from about 9% to about 30%. This confirms that a nail sample of status A is saturated with water.

Figure 5.15 Evolution of water content in nails against wetting time.

Figure 5.16 reveals the water-induced recovery when the temporary shape was stress-fixed ($\epsilon_U \approx 2.2\%$). A final R_r of about 100% demonstrates perfect water-induced SME in nail. The relationship between R_r and wetting time in Figure 5.16 shares the same trend as that between water content and wetting time in Figure 5.15. As the nail is programmed via bending, and water always penetrates from surface layer inward, shorter wetting time for “full” shape recovery than that for saturation with water is expected.

Figure 5.16 Evolution of shape recovery ratio R_r against wetting time in stress-fixed nail ($\epsilon_U \approx 2.2\%$).

Similarly, nail sample may be programmed by “water-fix” method. For instance, we may immerse a nail sample in room temperature distilled water for 60 minutes and then flatten it ($\epsilon_L \approx 2.3\%$) between two aluminum plates as mentioned in Section 5.2.2. After drying in room temperature air for 24 hours, the nail is in its temporary shape. Snapshots of shape change before and after programming and subsequent water-induced shape recovery are revealed in Figure 5.17. The average R_f is about 95%, which is close to that by “heating-fix”.

Figure 5.17 Snapshots of water-fix and water-induced shape recovery of nail.

Figure 5.18 reveals the evolution of R_r against wetting time in water-fixed nail. As compared with that in stress-fixed samples shown in Figure 5.16, the speed of shape recovery is a little bit slower. A relative higher internal stress in the intermediate

filaments (elastic component) in stress-fix ($\varepsilon_L=3.2\%\sim 3.5\%$ and $\varepsilon_U\approx 2.2\%$) might be the reason.

Figure 5.18 Water-induced shape recovery in water-fixed nail ($\varepsilon_U\approx 2.2\%$).

Figure 5.19 presents the evolution of surface strain and R_r in water-induced shape memory cycle in nail. In each cycle, the sample was water-fixed with a $\varepsilon_L\approx 2.3\%$ and then immersed in room temperature distilled water for 60 minutes. This procedure was repeated five times on the same piece of sample. It can be seen in Figure 5.19 that unrecoverable strain in water-induced SME in all cycles is always less than 0.1%, and R_r is always above 96%. When compared with cyclic heating-induced SME presented in Figure 5.7, the water-induced SME is almost fully repeatable without much notable deterioration.

Figure 5.19 Evolution of surface strain and R_r in cyclic water-induced SME in water-fixed nail.

5.4.2 Deformation by indentation

Figure 5.20 shows the typical loading/unloading curve of an indentation test on well-polished nail. The applied linear loading and unloading rate were 2 N/minute with 10 seconds pause time, the maximum load was 10.0 N, and contact force threshold was 0.01 N. The indenter is sphere-conical diamond with $R=200\ \mu\text{m}$ and $\alpha=90^\circ$. After indentation, the residual depth is about $23\ \mu\text{m}$. Figure 5.21 and Figure 5.22 present the 3D scanned images and cross sections at different stages, respectively.

Figure 5.20 Typical loading/unloading curve of indentation test on nail for water-induced SME.

Figure 5.21 3D scanned images of water-induced recovery in nail at microscopic scale. Left: 3D view; right: top view. (a) Original shape; (b) after indentation; (c) after 2 minutes in water; (d) after 5 minutes in water; (e) after 10 minutes in water.

Figure 5.22 Comparison of cross sections of microscopic water-induced SME in nail.

According to Figure 5.22, the maximum indentation depth is about 22 μm , which agrees with the result from micro hardness tester. After wetting in water for two minutes, significant recovery is observed. The maximum depth is reduced to about half only. Upon further wetting, the indent gradually disappears. Hardly any change can be observed after wetting for 10 minutes.

By applying Eqns (5.6), (5.7) and (5.8), we get the equivalent programming strain and residual strain after unloading as 15.15% and 9.49%, respectively. After immersing in water for 2, 5 and 10 minutes, the remaining equivalent strains are 6.99%, 5.19% and 0%, respectively. Hence, R_r is 100%, which agrees with that in macroscopic bending tests. A recoverable strain of about 9.5% is realized, which is higher than polycrystalline NiTi SMAs (about 6.7%) [3, 21, 79].

5.5 Multi-stimuli triple-shape memory effect

In above experiments, programming was done by either stressing at room temperature or high temperature, or deforming a wet sample and then drying it. Both water and heat may be used as the stimulus for shape recovery. Figure 5.23 shows the evolution of R_r in three water-fixed nail samples upon gradual heating. Apparently, R_r is tiny. On the other hand, Figure 5.24 shows that almost full shape recovery can be realized

by wetting even the temporary shape is heating-fixed. Hence, water is effective for both programming and shape recovery, while heat is not.

Figure 5.23 R_r of water-fixed nails upon heating ($\epsilon_L \approx 2.3\%$, $\epsilon_U \approx 2.2\%$).

Figure 5.24 R_r of water-induced SME in heating-fixed nails ($\epsilon_L \approx 2.3\%$, $\epsilon_U \approx 2.1\%$).

A few additional tests were conducted using 20% water content nail samples, which were obtained by wetting the original samples in room temperature distilled water for five minutes. At $\epsilon_L \approx 2.3\%$, the average R_r of stress-fix is 14.2%, while that of 9% water content samples (original samples as in Section 5.3) is 21.1%. Average R_r for 20% water content samples in heating-induced SME ($\epsilon_U \approx 2.2\%$) is 52.6%, as compared with 32.0% for 9% water content samples. It is clear that the exact water content of nail effectively influences its SME properties.

Based on above experimental results, the triple-SME may be achieved in nail using multi-stimuli. Figure 5.25 presents a one-step programming strategy, which is to flatten a piece of nail directly (stress-fix, $\epsilon_L \approx 3.0\%$). After heating for shape recovery, R_r is only around 30%. The resulted shape is then thermal stabilized. Upon subsequent wetting in water, R_r reached over 95%. We may conclude that after programming, the plastic deformation in the intermediate filaments (elastic component) is limited, and only water is able to effectively get rid of the quasi-plastic deformation in the matrix (transition component).

Figure 5.25 Snapshots of one-step programming triple-SME in nail. (a) Original shape; (b) stress-fixed temporary shape; (c) after heating to 80°C (relative humidity 50%) for 5 minutes; (d) after immersing in room temperature distilled water for 30 minutes.

An alternative approach to achieve the triple-SME in nail is to dry a piece of saturated nail sample with constraint in air for a shorter period of time during water-fix programming, e.g., two hours instead of 24 hours as applied in Section 5.4.1. Therefore, water content of nail decreases from 30% to about 20%. The partial water-fixed shape is shown in Figure 5.26(b). After being manually twisted, the twisted shape is largely maintained as shown in Figure 5.26(c). In the recovery process, heating is applied first, and the twisting deformation is largely removed, while the bending deformation still remains, as can be seen in Figure 5.26(d). It confirms that heating has limited effect on the previous deformation fixed by water. Only wetting in water results in almost full recovery, as demonstrated in Figure 5.26(e).

Figure 5.26 Snapshots of two-step programmed triple-SME in nail. (a) Original shape; (b) flattened ($\epsilon_L \approx 2.3\%$) and dried in room temperature air for two hours; (c) after manually twisted; (d) heated to 60°C (relative humidity 50%) for 5 minutes; (e) immersed in room temperature distilled water for 30 minutes.

The advantage of the two-step process over one-step process is that the intermediate shape (Figure 5.26b and d) is more controllable and predictable.

5.6 Conditions and mechanism of shape memory effect

The influence of denaturation on the SME performances of nail was investigated. Nail samples were placed in distilled boiling water (100°C) for 30 minutes, followed by natural drying in room temperature air for 24 hours, and their water contents came back to around 9%. According to Figure 5.12, 100°C is enough to denaturalize wet nail with high water content.

Figure 5.27 reveals both heating-induced and water-induced SME in denatured nail, in which the temporary shapes were stress-fixed. It is clear that for in both cases, shape recovery is about the same as that of original samples. Hence, we may conclude that neither heating-induced SME nor water-induced SME in nail keratin is associated with protein denaturation.

Figure 5.27 Snapshots of shape recovery in denatured nail. (a) Heating-induced SME $\epsilon_L \approx 3.0\%$, $R_f \approx 30\%$; (b) water-induced SME in room temperature, $\epsilon_L \approx 4.2\%$, $R_f \approx 94\%$.

As mentioned in Chapter 2, the absorption of water is able to decrease the T_g of, for example, polyurethane, to lower than the room temperature for the SME [39, 49, 50]. According to the DSC results reported in Figure 5.2 and Figure 5.12, T_g is decreased

about 24°C in fully wetted nail, which is due to the strong plasticizing effect of water [222], but it is still much higher than room temperature.

As such, a series of water-fix and water recovery tests were conducted in which environment temperature was controlled to be around 0°C using iced water for wetting and drying in a 0°C ice box to ensure that the only variable here is water content. Figure 5.28 presents the sequence of shape recovery in terms of R_r in iced water. As we can see, after 90 minutes, R_r is over 90%, so that we may conclude that the wetting for water other than environment temperature is the main reason for the water-induced SME. Swelling might be one possible factor that promotes the SME [103]. Since the movement of water molecular is less active at lower temperatures, the recovery speed at around 0°C is slower than that in room temperature (25°C).

Figure 5.28 Water-induced recovery of nail in iced water. Temporary shape ($\epsilon_U \approx 2.2\%$) is fixed by iced water as well.

It should be noted that deformation during programming may be in any direction. For instance, if a nail sample is further bent inward for “U” shape instead of flattening and then water-fixed, wetting in water results in almost full shape recovery of this temporary shape, as shown in Figure 5.29. As such, the SME discussed here should not be ascribed to different layered properties of nail.

Figure 5.29 Water-induced recovery in a “U” shaped nail.

It is known that for polymeric materials, the basic mechanism for the SME may be classified into two main categories, one is dual-state, and the other one is dual-component [55, 56]. Based on the two-phase structure of keratin [159], and the SME performance discussed above, we may conclude that the SME in nail is under the dual-component category.

Previous studies revealed that keratin protein is essentially a two-component system, which includes intermediate filament around 10 nm wide and amorphous matrix [161, 239]. The matrix is hydration sensitive, and its modulus and yield stress drops at the presence of water [240]. On the other hand, intermediate filaments remain stiff even when they are immersed into water. This is essentially a system for the dual-component mechanism for the SME, in which intermediate filament serves as the elastic component, and matrix functions as the transition component. Intermediate filaments may keep their elasticity within the whole working process, while matrix changes its modulus dramatically when a right stimulus, such as water, is applied [159].

At room temperature, as both intermediate filament and amorphous matrix are highly elastic at small strain, the majority of mechanical deformation instantly recovers upon removal of the applied external load, which attributes to a lower R_f in stress-fix method. For example, if a piece of nail sample is programmed by means of stress-fix and ε_L is about 2.3%, the average R_f is only 21.1%. While for the same programming

parameters, the average R_f for heating-fix and water-fix are 93.4% and 95.3%, respectively. Higher residual strain is the result of plastic and/or quasi-plastic deformation of intermediate filament upon deformation at high temperatures or after wetting.

At high temperatures, glass transition occurs and the intermediate filament (transition component) softens. Upon deformation, elastic energy is stored in the matrix (elastic component). Transition component becomes hard again upon cooling back to room temperature, which freezes the temporary shape. Therefore, heating-fix method has a higher R_f .

Basically, water content serves the same function as heat, which is further verified by the compression test as illustrated in Figure 5.30 (inset). Due to the nature of a curved shape, the test is essentially a bending test. The same piece of nail sample was used, however with different water content in each test. A small pre-compression of 0.1 mm was applied on sample to prevent the nail from slipping. In each test, the maximum compression displacement was 4 mm. As we can see, in all five tests, the residual strains are almost zero. As such, compression to a maximum displacement of 4 mm is confirmed to be within the elastic range.

Figure 5.30 Bending tests of nail at different water contents.

With the increase of water content, the stiffness of nail gradually decreases. Water content determines the stability of hydrogen bond in the matrix structure of nail keratin [168], and thus it directly influences physical properties of nail [235]. On the other hand, the intermediate filaments does not interact with water and its modulus remains unaffected [166, 168]. Therefore, at high water content, the nail is more rubber-like in response to external loading force.

Figure 5.31 qualitatively summarizes the water content dependent response of nail, in which B is for the nail in normal conditions (water content 9%; environment relative humidity 60%~70%, room temperature 25°C). In its dry state, e.g., heating to 100°C in air (relative humidity 50%) for 30 minutes, it becomes A, which is brittle and easy to break. This is the status with 0% water content. Irreversible change has been made, so that no more shape memory phenomenon can be observed. On the other hand, if B is immersed in room temperature distilled water for 60 minutes, it becomes C with about 30% water content. The transition between B and C is fully reversible, upon wetting or drying.

Figure 5.31 Schematic illustration of effect of water content on the SME behavior of nail.

By means of either stress-fix or heating-fix, B can be deformed to B'. The temporary shape is able to sustain unless a right external stimulus is applied. For the heating-induced SME, B' returns back to B with a relative lower R_r ; for the water-induced SME, B' changes to C, and the corresponding R_r is close to 100%.

If water content is increased, above phenomena still exist. However, with a the higher water content, R_f is lower in stress-fixed programming, and R_r is higher in heating-induced SME. This is because the transition component of nail becomes softer gradually with the increased water content.

C is for the status that nail has very high water content (about 30%), and responses to external loading in a rubber-like manner. As such, the transition between C and C' belongs to the shape change effect. In order to fix the temporary shape C', water-fix method has to be used. After drying, C' becomes B'. Wetting B' results in C via the water-induced SME. If B' is obtained from C' (rather than B), heating-induced shape recovery from B' to B is weak, as indicated in Figure 5.23. Moreover, even B' is obtained from B but via heating-fix (rather than stress-fix), subsequent heating-

induced shape recovery also has a low R_r , as indicated in Figure 5.6, since water content has decreased during the heating-fix process, and lower water content results in lower R_r of heating-induced SME. Among all programming and recovery methods, water-fix and water recovery always have the highest R_f and R_r .

Although R_r in heating-induced SME is relatively low, the remaining unrecovered strain is almost fully recoverable by wetting in water, as shown in Figure 5.25. It might be because water is able to disrupt the hydrogen bond in matrix due to the strong plasticizing effect of water [164-167], but moderate heating (to 80°C) cannot. That is also the reason why heating (to 80°C) has minor effect on water-fixed B' . However, severe heating (to over 100°C) leads to irreversible structure change of other part that the whole material is broken.

5.7 Summary

In this chapter, the SME in nail keratin is investigated under various conditions. It proves that both heat and water can serve as the stimuli to trigger SME, the underlying mechanism of which is dual-component principle. Moreover, the SME performances, i.e., R_f and R_r , are heavily dependent on the exact water content. By utilizing both stimuli, we are able to realize even the triple-SME in one single piece of nail keratin.

Chapter 6 Shape Memory Effect in Silkworm Silk

We have investigated the shape memory effect (SME), both heating-induced and water-induced, in human nail in Chapter 5. In this chapter, we follow the similar procedure as reported in Chapter 5 to study the SME in silkworm silk, which is also within the same family of natural keratins as nail. However, unlike that of nail, which has an irregular shape, silk is in a rather uniform fiber shape. Hence, silk is convenient for more accurate characterization.

Besides, the actual water content of silk at different stages was determined. Uniaxial tensile and relaxing tests, which are not easily applicable to nail, were performed. Consequently, the SME in silk was accurately characterized by means of the change in elongation. After these, we can compare the shape memory performance of natural keratin with that of common engineering shape memory polymers.

6.1 Materials

Silkworm cocoon is a protective shell produced by silkworm caterpillar during its metamorphosis. It is made of a single continuous silk thread which has a length of 1000~1500 meters [241]. A piece of raw silk thread consists of two types of proteins, namely sericin and fibroin. The former is a layer of outside coating. It is usually removed for the convenience of dyeing by means of dissolving in 100°C water, a procedure known as degumming in the industry [242, 243]. The latter is insoluble in most solvents, and remains after degumming [244]. The silk fibroin is β -keratin. Its mechanical properties are determined by its two components, namely matrix and intermediate filaments, which are embedded within the matrix [245].

Because of its excellent mechanical properties [241, 246], absence of toxicity [247] and biodegradability [248], silkworm silk has been extensively investigated and already implemented as a biomedical material in tissue engineering [244, 249]. Typical applications include silk-based scaffold and suture [244, 250].

Same as in nail, the matrix/intermediate filaments structure of silk implies the possibility to realize the SME based on dual-component principle.

The silkworm silk cocoons (Figure 6.1 left) were obtained from Jiang Su University, P.R. China. Silk wire (Figure 6.1 right) was purchased from Huzhou Sentong Silk Weaving Co., Ltd, P.R. China. To demonstrate the water-induced SME in silk cocoons, we conducted a similar bending test as that for nail. A piece of sample, which is about $30 \times 10 \text{ mm}^2$ in size, with a thickness of about 0.4 mm, was cut out from a silk cocoon (Figure 6.2a). After wetting in room temperature distilled water for 120 minutes, it was flattened between two aluminum plates of 3 mm in thickness and clamped by two clips with a force about 20 N. The flattened shape (Figure 6.2b) recovers its original shape after wetting in room temperature distilled water for 30 minutes (Figure 6.2c). The recoverable surface strain in the process is about 1%.

Figure 6.1 Typical silk cocoons (left) and commercial silk wire (right).

Figure 6.2 Snapshots of water-induced SME in silk cocoon. (a) Original; (b) after flattening and drying in air for 180 minutes (c) after wetting in water for 30 minutes.

Figure 6.3 demonstrates the water-induced SME in silk wire. As received silk wire was wound around a 3 mm diameter cylinder followed by the water-fix procedure, i.e., deforming wetted silk wire and then drying it in room temperature air with the temporary shape fixed, which resulted in a silk coil. The silk coil was cut into two pieces. One piece was immersed in room temperature distilled water, in which the coil shape disappeared quickly. The other piece was first heated to 80°C in air (relative humidity 50%). It reshaped slightly. Wetting in water fully uncoiled the temporary shape. It should be pointed out that the swelling ratio of silk wire is quite limited. In this silk, it is less than 0.1%.

Figure 6.3 Water-induced SME in silk wire [55].

Above tests clearly demonstrate the water-induced SME in both silk cocoons and wire. Since nail keratin reveals better shape memory performance if programmed and activated by water, in this study we focus on the effect of water on the thermo-mechanical properties of silk, in particular silk wire.

A close look reveals that, in fact, each piece of as-received silk wire is consisted of two bundles twisted together. Further observation via scanning electron microscope (SEM) (JEOL JSM-5600LV) shows that each bundle is formed by ten thinner fibers (Figure 6.4a). Figure 6.4(b) reveals that, same as that reported in the literature [251], the diameter of such fiber is about 10 μm . Although the real cross section of a fiber may not be a perfect circle [251], we may still consider it in this way for simplicity. As such, the cross-sectional area of a single silk wire is about $1.57 \times 10^{-9} \text{ m}^2$.

Figure 6.5 presents the thermal gravimetric analysis (TGA) result of as received silk wire, which was heated from room temperature (about 25°C) to 800°C at a heating rate of 10°C/min. Similar to that of nail keratin (Figure 5.1), the highest decomposition rate appears at around 300°C, and the residual weight is about 20% at 800°C.

Figure 6.4 SEM images of (a) a single piece of bundle and (b) a single piece of fiber.

Figure 6.5 TGA result of silk wire at a heating rate of 10°C/min.

6.2 Effect of water content

After heating in 80°C air (relative humidity 50%) for 30 minutes, as received silk wire lost about 2.1% of its original weight. We regard such a piece of silk wire as “fully dried”. Therefore, the water content of as-received silk wire is about 2.1%.

Figure 6.6 plots the evolution of water content in as received silk wire when subject to wetting in distilled water and drying in air (relative humidity 60%~70%) at room temperature (about 25°C) for different period of time. About 100 mg of sample was used in each test and six tests were conducted using different pieces of samples.

Figure 6.6 Evolution of water content in silk wire upon wetting in water and then drying in air.

It is clear that due to a high surface/volume ratio of thin wires, the speed of water absorption is much higher in silk than that in nail. As we can see, water content increases rapidly to over 40% in the first two minutes. Upon wetting in water for 120 minutes, water content reaches about 60% and virtually becomes stable. Subsequently, after 60 minutes of drying, the water content drops back to less than 3%. Same as that in nail keratin, this wetting/drying process is repeatable.

In the following discussion, unless otherwise stated, SW2 and SW50 are meant for as received silk wire (about 2% water content) and silk wire which has been immersed in room temperature distilled water for 5 minutes (about 50% water content), respectively.

Figure 6.7 presents differential scanning calorimetry (DSC) results of SW2 and SW50. The T_g of SW2 is about 56°C as marked. For SW50, it is hard to spot a typical T_g in the heating process of the first cycle. The wide trough around 90°C indicates evaporation of water, similar to that in nail shown in Figure 5.12. The heating result of the second cycle of wet silk is almost a straight line without any visible transition. It is suggested that silk keratin is denatured upon heating to 160°C and this process is irreversible.

Figure 6.7 DSC results of SW2 and SW50 at a heating/cooling rate of 10°C/min.

Since the cross-sectional area of a single silk wire is small, a customized setup, which is schematically illustrated in Figure 6.8, was used for mechanical testing. A silk wire was wound around two steel cylinders (radius 7.5 mm) for 16 loops and a knot was tied. Since the maximum strain of silk wire due to bending around the cylinder is less than 0.07%, its influence may be neglected. The gauge length L (ranged from 250 to 300 mm) was determined as the central distance between two cylinders. A constant strain rate of 3.33×10^{-4} /s was applied in loading and unloading.

Figure 6.8 Illustration of setup for tensile test of silk wire.

Figure 6.9(a) reveals that the strains at break for SW2 and SW50 are 11.5% and 12.7%, respectively; and the corresponding stresses are 225 MPa and 200 MPa respectively, which are close to that reported in the literature (230 ± 10 MPa stress) [252]. Note that the point of fracture upon loading did not occur at the knot. In Figure 6.9(b), the upper limit of tensile strain was set as 8% to avoid fracture. The tensile Young's modulus (E), which is calculated from the slope in the early stage of unloading process, is about 13.0 GPa for SW2 and 10.7 GPa for SW50.

Figure 6.9 Tensile tests of silk wire. (a) Stretch to fracture; (b) stretch to 8% strain.

It is suggested that water increases the ductility of silk wire, however such a effect is not very much significant. The loading curves of SW2 in both Figure 6.9(a) and (b) can be categorized into two regimes where different slopes are exhibited. The first one is before 2% strain and the second one is after 2%. Such a change is mainly due to the α -helix to β -sheet transition in the intermediate filaments [253-255]. The loading curve of SW50 seems to have a more stable slope because absorbed water has changed the structure of matrix, which is held together mainly by hydrogen bonding [245]. Therefore, the α -helix to β -sheet transition is hindered in some extent as the unfolding of α -helix is kinetically impeded by the matrix [158]. Note that since the applied strain rate was 3.33×10^{-4} /s, it took about 4 minutes to stretch the silk wires to

8% strain. Following the trend revealed in Figure 6.6, even within 4 minutes, the actual water content in silk wires might be reduced to about half only.

Figure 6.10 presents the results of cyclic tensile tests on silk wires with 2% strain increment in each cycle. The evolution of E is summarized in Figure 6.11. As we can see, E is always around 12.9 GPa in SW2. Note that previously reported values vary from 8 to 16 GPa [252, 256-259]. However, E of SW50 keeps on increasing with the increase of strain until it is almost doubled (around 11 GPa) at about 6% strain. Afterward it becomes stable, but is still slightly lower than that of SW2, which may be due to two reasons, the water content of SW50 at 6-8% strain is still more than 2%, and the stretching/drying process may result in a slightly different micro-structure, in particular in the matrix, as compared with that of SW2 by stretching only. At this point we may conclude that drying is the major reason for the increase of E in SW50 upon cyclic stretching and the Young's modulus of *dry* silk is about a constant.

Figure 6.10 Cyclic tensile testing results of (a) SW2 and (b) SW50.

Figure 6.11 Evolution of E of silk wire.

Figure 6.12 plots the relaxation testing results of both SW2 and SW50. Two different strains, namely 8% and 2%, were applied. Note that according to Figure 6.6, the water content of SW50 drops back to about 3% after drying in room temperature air for one hour. In both tests, after an initial sharp drop due to relaxation in both the matrix (transition component) and intermediate filaments (elastic component), the stress in SW2 approaches a constant. A closer look of Figure 6.12(b) reveals that actually the stress still decreases, but at a very low speed, until about 35 minutes. After that the stress starts to increase almost monotonically, but only very slightly, which indicates the influence of drying induced shrinkage starts to take leading role.

Figure 6.12 Relaxation in silk wire. (a) Stretched to 8% strain and held for 30 minutes; (b) stretched to 2% strain and held for 60 minutes.

On the other hand, after a sharp drop, the stress in SW50 gradually decreases due to the continuous evaporation of water. As the water content is much higher than that in SW2, the influence of water evaporation in the early stage (till about 40 minutes) on the stress can be easily observed, i.e., within this period, water induced shape fixity results in remarkable and continuous drop in stress. Same as that in SW2, drying induced shrinkage starts to become noticeable only after about 40 minutes, evidenced by a slower dropping speed in stress.

Recall Figure 6.11 and the discussion about the possible reasons for the difference in the Young's modulus between SW2 and SW50 at 6-8% strain. The observed far greater drop in stress in SW50 provides good evidence to support the existence of different microstructures in the matrix after stretching/drying or stretching only.

6.3 Water-induced shape memory effect

The shape memory performance of silkworm silk wire is evaluated by two standard parameters of R_f and R_r . As received silk wire was cut into pieces with an initial length of 200~250 mm. After being stretched to 8% strain, the average residual strain is around 4.8%, which indicates a R_f of about 60%. The stretched silk wire was then wetted for 30 minutes in room temperature distilled water. The resulted average R_r is about 63%, which is not as good as that in nail keratin. For comparison, the average R_r of heating-induced SME, which was conducted by heating the same batch of pre-stretched silk wire to 80°C in air (relative humidity 50%), is about 28%.

We have also conducted experiments following the water-fix method as discussed in Chapter 5. Two different maximum tensile strains were used, namely 2% and 8%. The results are listed in Table 6.1. When compared with stress-fix, a higher R_f is achieved by the water-fix method, as more deformation can be locked during hardening of the

matrix. Furthermore, as shown in Figure 6.9 and Figure 6.10, the softening effect of water is more efficient at 2% strain than that of 8% strain. Therefore, higher ratio of quasi-plastic deformation of the matrix is induced. As a result, for the water-fix method, R_f of 2% programming strain is higher than that of 8% programming strain.

As for shape recovery, wetting in water is more effective than heating for a higher R_r because of the strong plasticizing effect of water on hydrogen bond of matrix [164-167]. Also, as expected, 2% programming strain produces a higher R_r than that of 8% programming strain by water-fix and water recovery method. Larger plastic deformation in the intermediate filaments upon larger straining should be the main reason. Note that due to low R_f by stress-fix, corresponding R_r of 2% programming strain cannot be accurately determined, and thus no reliable results were obtained so far.

Table 6.1 The SME of silk wire under different programming and stimulus conditions.

Maximum strain in programming	R_f		R_r		
	Stress	Water	Stress-Heat	Stress-Water	Water-Water
2%	23 $\pm$ 2%	90 $\pm$ 3%	*	*	87 $\pm$ 2%
8%	60 $\pm$ 3%	80 $\pm$ 1%	28 $\pm$ 3%	63 $\pm$ 6%	75 $\pm$ 6%

* Measurement error is too significant.

Since water-induced SME is observed in both human nail and silkworm silk wire, which has a two-component keratin protein structure, it is nature to deduce that similar phenomenon should be applicable to other bio-materials that share a common structure. Actually, preliminary result indicates that human hair, whose main component is also keratin, can exhibit shape memory effect using water-programming and water-recovery procedure. It implies that shape memory effect could be a generic

phenomenon among keratin or even other types of bio-materials, based on dual-component mechanism.

6.4 Summary

We have demonstrated that the SME, especially induced by water, is also achievable in another keratin protein, namely silkworm silk. The effects of water on the performances of silk wire in tension, namely the strain vs. stress relationship, evolution of Young's modulus, and relaxation, are investigated. The softening and hardening of matrix, which is the transition component in silk, due to the change of water content is believed to be the main reason of the above mentioned phenomena.

As compared with common engineering SMPs, which usual have a recovery strain at 100% scale, the recovery stain of silk wire is much less, only around 5~6%. However, 5~6% is comparable to the maximum recovery strain of shape memory alloys. Keratin, as a kind of protein, has the intrinsic advantages in biomedical applications, such as biocompatible and biodegradable.

Chapter 7 Conclusions and Future Works

7.1 Conclusions

In this dissertation, current status of shape memory materials relevant to this study is reviewed, including the underlying mechanisms for the shape memory effect (SME) and some novel applications of shape memory materials.

Based on a series of DSC tests, the mechanism of the temperature memory effect (TME) in NiTi shape memory alloys (SMAs) is further investigated, from the energy point of view. In the case of single temperature interruption, in order to have two separate troughs in final heating, the *newly* formed martensite M2 should nucleate at the interphase of austenite and *old* martensite M1, where the existing elastic energy drives the transition.

We further explore the TME in all other possible situations in NiTi SMAs with/without R-phase. It is demonstrated that the TME can be utilized as the mechanism for temperature sensors. An accuracy of $\pm 0.5^{\circ}\text{C}$ is achievable to monitor the actual over-heating temperature using m-TME II.

The triple-shape memory effect (triple-SME), which is about an intrinsic feature of SMPs, is realized in NiTi SMAs, most likely, for the first time. Two programming approaches, namely small strain program (SSP) and large strain program (LSP), are proposed without introducing a gradient transition temperature field in the length direction of NiTi SMA samples.

In order to produce significant triple-SME in a NiTi SMA, there are certain conditions on the material and the programming procedure. R-phase is a must in addition to austenite and martensite. The associated two transitions upon heating (namely R-phase to austenite, and martensite to austenite) should be well separated (material property) and significant enough (may be optimized by programming).

The main difference between SSP and LSP is that martensite is thermo-induced in SSP, while in LSP it is stress-induced. LSP should be more practically useful as the recoverable strain is far greater than that in SSP. The influence of programming parameters on the triple-SME is systematically studied for LSP.

The SME in human nails and silkworm silk (keratin protein is their main component), is systematically investigated. For both materials, the SME can be triggered by heating; however, the corresponding shape fixity ratio (R_f) and shape recovery ratio (R_r) are low. On the other hand, water is far more effective for shape fixing and shape recovery. Both corresponding R_f and R_r are above 95%.

According to the intermediate filaments/matrix model of keratin structure, the mechanism for the SME in keratin is dual-component mechanism. Strong plasticizing effect of water on the matrix is the main factor that attributes to the SME in keratin. We also demonstrate that the actual performance of SME in keratin is heavily dependent on the actual water content. As shown, the triple-SME is achievable utilizing multiple stimuli in a couple of ways.

7.2 Future works

The mechanism for the TME reported here is based on *non-direct* experimental observation. It is difficult, but yet worth wise, to confirm this mechanism via direct

experimental study. The SMA temperature sensor reported here is only focused on over-heating applications, while the possibility for over-cooling applications is merely mentioned. A systematic investigation may be conducted in a similar way to explore further.

The study of natural bio-polymers is currently the focus for the next generation of polymeric materials. The SME, which has been extensively studied but mostly in traditional polymers so far, should be expanded to those materials as well. The work reported in Chapters 5 and 6 of this dissertation is a small step toward this direction. As for future works, the following are recommended,

- To understand the fundamentals of the SME in keratin and identify the essential difference between heat and water induced SMEs from bio-chemical structure point of view;
- To explore the potential applications of keratin based on its SME, especially in bio-medical engineering;
- To investigate the influential factors that might affect the shape memory performance of keratin, and the possibility of utilizing other types of stimulus, such as enzyme;
- To examine the reliability of the SME of keratin in vivo and in vitro, which is essential for bio-medical applications;
- To study the SME in other kinds of natural bio-polymers, such as DNA.

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List of Publications

1. C. Tang, W.M. Huang, C.C. Wang, H. Purnawali, The triple-shape memory effect in NiTi shape memory alloys. *Smart Materials and Structures*, 2012, 21(8):085022.
2. C. Tang, W.M. Huang, From dual-shape/temperature memory effect to triple-shape memory effect in NiTi shape memory alloys. *Advances in Science and Technology*, 2013, 78:1-6.
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