Thermally induced fracture and thermomechanical properties of NI-MN-GA-FSMA single crystals

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**THERMALLY INDUCED FRACTURE AND
THERMOMECHANICAL PROPERTIES OF NI-MN-
GA FSMA SINGLE CRYSTALS**

XIONG FENG

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2008

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School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
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by

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Supervisor: A/P Liu Yong

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Abstract

Ni-Mn-Ga ferromagnetic shape memory alloys (FSMAs) have attracted considerable attentions since they can provide large strain output and quick response simultaneously. In this research, thermomechanical behavior and thermally induced fracture of single crystal Ni-Mn-Ga FSMAs were investigated.

Ni-Mn-Ga FSMAs exhibited the two way memory effect (TWME) during thermal cycling; however, it was discovered that the stability of TWME is very sensitive to the temperature rate and external load. The martensite strain can change from contraction to elongation, or vice versa, during thermal cycling. The irregularity in the strain change is a result of the internal stress-induced redistribution of martensite variants during forward transformation. The internal stresses are accumulated during thermal cycling and have the magnitudes comparable to the critical stress needed to reorient the twin variants (1~3 MPa).

The thermomechanical fatigue property of Ni-Mn-Ga FSMAs is investigated. The crack propagation behavior is strongly related to the forward transformation and the martensitic twin structure. Cracks prefer to propagate along the twin boundaries as well as twin-twin intersections through multiple propagation modes. It was also found that high temperature rate during thermal cycling reduces the fatigue resistance of Ni-Mn-Ga FSMAs.

Theoretical analysis on the thermally induced fracture behavior of Ni-Mn-Ga FSMA was performed in the framework of elastic-plastic fracture mechanics. The results show that the primary reason for the thermally induced fracture in Ni-Mn-Ga FSMAs is the increase in the crack tip stress intensity factor (SIF) due to stress redistribution around the crack tip as a result of stress-induced martensitic (SIM) transformation. With lowering the temperature to approach to the martensite start temperature, the crack tip SIF of Ni-Mn-Ga

FSMA increases significantly, being very different from that of Ni-Ti and Cu-Al-Ni SMAs. The sensitive temperature dependence of crack tip SIF in Ni-Mn-Ga is responsible for its brittleness under thermal cycling and is strongly related to the yield stress, temperature dependence of the critical stress for SIM transformation and transformation interval. Based on the present analysis, the effect of temperature rate on the fatigue property of Ni-Mn-Ga FSMA is also explained.

List of Publications

1. F. Xiong, Y. Liu, and E. Pagounis, Fracture mechanism of a Ni–Mn–Ga ferromagnetic shape memory alloy single crystal, *Journal of Magnetism and Magnetic Materials*, 285 (2005) 410–416;
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4. F. Xiong and Y. Liu, Effect of stress induced phase transformation on the crack tip stress intensity factor in Ni–Mn–Ga shape memory alloys, *Acta Materialia*, 55 (2007) 5621–5629.

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Chapter 1 Introduction

1.1. Background

Smart materials can "remember" the structural configurations and conform to them after severe deformation when given a specific stimulus, such as temperature, stress, or electric and magnetic fields [1]. They are ideal for machine design in a wide range of medical, defense and industrial applications with high reliability, low power requirement and flexible controllability. Smart materials can be classified into several types according to their deformation mechanisms; however, in certain cases, the engineering applications are limited by some intrinsic characteristics, for example, the inefficient response (especially in cooling) in the conventional thermally active shape memory alloys (SMAs), or small strain output [2, 3] in the magnetostrictive materials. Thus, ferromagnetic shape memory alloys (FSMAs) have attracted considerable attentions since it was discovered in 1996 in a Ni_2MnGa single crystal [4, 5]. Large strain output (up to 10% [6, 7]) and quick response (less than 1 μs [8]) are simultaneously provided with a magnetic shape memory (MSM) effect, in which the martensite variant boundaries motion is driven by the large magnetocrystalline anisotropy [5, 9].

At the present time, Ni-Mn-Ga alloy system is considered as the only candidate of FSMAs for applications. MSM effect has also been observed in some other alloy systems, such as Fe-Pd [10-13], Fe-Pt [14, 15], Ni-Mn-Al [16-18], Co-Ni-Ga [19-22], Co-Ni-Al [23-27], Ni-Fe-Ga [28-31], Co-Ni [32, 33], and etc. However, iron based FSMAs, with a strain of < 1% under ~10 kOe magnetic field at room temperature, are uneconomical for industrial

applications due to the high cost of precious metals. Co-Ni-Al alloys, as well as the Ni-Mn-Al alloys, have considerable magnetic anisotropy energy (3.9×10^6 erg/cm³) and sufficient ductility, but the reversible magnetic field induced strain (MFIS) is rather small, in the order of $\sim 0.1\%$. As for the Co-Ni-Ga and Ni-Ga-Fe alloys, some physical phenomena related to the MSM effect have been noticed; however, the most important MFIS information is lacked. A Co-Ni single crystal shows one-time strain of 3% under a 2 T magnetic field, but the martensitic transformation temperatures are far below room temperature. Besides, few experimental results are available about the mechanical and magnetic properties in these alloys. Comparatively, it has been confirmed by many research groups that the Ni-Mn-Ga FSMA exhibit large recoverable strains under a modest magnetic field of 0.4~0.6 T. The transformation temperatures are controllable by changing the chemical composition, ranging from about 100 K to more than 550 K, and the cost is intermediate. Hundreds of research papers, as well as several good reviews [34-37], have been published both experimentally and theoretically. The progress of recent investigations on the Ni-Mn-Ga FSMA will be described in Chapter 2.

One serious drawback for the engineering applications of Ni-Mn-Ga FSMA is the poor fatigue property. The polycrystalline Ni-Mn-Ga alloys begin to fracture before obtaining a MFIS of 0.5% during cyclic deformation [38]. In single crystals, the fatigue properties are strongly dependent on the magnitude of MFIS during magnetic cycling [39, 40]. It seems that there is a ductile-to-brittle transition with increasing the MFIS in the Ni-Mn-Ga FSMA. The alloys with *5M* or *7M* structures can survive millions of magnetic cycles under small MFIS ($< 2\%$); however, the fatigue life drops to a few thousand with larger strains ($\sim 6\%$). What's more, Ni-Mn-Ga FSMA are prone to fracture under thermal cycling through the phase transformation temperatures. This phenomenon is very different

from other SMAs having thermoelastic phase transformations. For example, typical SMAs like NiTi have a much longer fatigue life ($\sim 10^7$) with cyclic deformation (strain $> 2\%$).

To fully exploit the practical application of FSMAs, it is necessary to study their failure mechanism under cyclic deformation. However, only a few studies in this field have been attempted in the last decade. The instinct brittleness in the polycrystalline Ni-Mn-Ga alloys are due to crack formation at the grain boundaries even in the high temperature [38]. In Ni-Mn-Ga single crystals, cleavage fracture on the $\{110\}_c$ planes has been considered as the main failure mode, and was also noticed in the present work, based on the observation of the typical river patterns on the fracture surface [41]. It indicates that this material has a low resistance to the tensile stress acting normal to its cleavage planes $\{110\}_c$, which are also the twin planes considered by many researchers [42-47]. Thus, the fracture failure in the Ni-Mn-Ga FSMAs is closely related to its martensitic structure. A simple model [41] was proposed that local stresses build up when a barrier twin blocks a twin lamella and consequently cause the nucleation of a crack on the habit plane of the barrier twin, and results in the cleavage-like fracture. On the other hand, to date, thermally-induced fracture in Ni-Mn-Ga FSMAs is seldom reported [48, 49].

1.2. Objective and scope

The aim of the present research is to investigate the fracture mechanism and cracks formation and propagation behaviors in Ni-Mn-Ga single crystals under thermal cycling. Major attention is paid to the thermomechanical fatigue. However, the degradation of SME, which is also termed as shape memory fatigue [50], i.e. transformation temperatures

shift and shape memory strain reduction, is also studied through the thermomechanical analysis. The scopes include

- Material properties characterization

Combining variant boundary motion with ferromagnetism in the martensitic state, the MSM effect provides a manner to control the shape memory properties with the rearrangement of martensitic variants by applying magnetic fields. The magnetic field can also influence the martensitic transition and magnetization during thermo-/magneto-mechanical experiments. The intention was to ensure that the Ni-Mn-Ga single crystals can exhibit the MSM effect. The crystal structural and thermal, magnetic and mechanical properties of the Ni-Mn-Ga FSMAs were investigated.

- Thermomechanical stability

Except for the MSM effect, Ni-Mn-Ga FSMAs also exhibit two-way memory effect (TWME) during thermal cycling with large deformation strains. However, it was reported recently that during some stress-free thermal cycles, the shape memory strain of Ni-Mn-Ga FSMAs suddenly changed from elongation to contraction or vice versa, which was explained as a result of the change in the internal stress field but not in details [51, 52]. Such abnormal phenomenon has been seldom observed in other types of SMAs. Thus, the TWME of Ni-Mn-Ga single crystal under different thermomechanical conditions was investigated. The internal stress was estimated based on the change in M_s according to the modified Clausius-Clapeyron equation. The factors affecting the internal stress field and the stability of TWME were studied.

- Fatigue in the Ni-Mn-Ga FSMA

The classic mechanical fatigue is the progressive, localized and permanent structural damage when the material is subjected to cyclic loading while the applied stresses are much lower than the yield stress. It includes the accumulation of defects, crack initiation and propagation, and catastrophic failure. Compared to other SMAs, the ‘brittle’ Ni-Mn-Ga FSMA shows much weaker fatigue property and the material is prone to break under thermal cycling. To understand the crack initiation and propagation behaviors in Ni-Mn-Ga FSMA, microscopic observations were carried out on the martensite morphologies of the surface and fracture planes. Particularly, attentions were paid to the effects of phase transformations, temperature rate during thermal cycling, and coexisting of differently oriented twin variants on the fatigue property of the Ni-Mn-Ga FSMA.

- Effect of SIM transformation on the crack tip SIF

In this section, the effect of stress-induced martensitic (SIM) transformation on the crack tip stress intensity factor (SIF) was investigated through examining the stress redistribution around the crack tip and its effect on the plastic zone size. As a result, the temperature dependence of crack tip SIF due to localized SIM transformation was established. In addition, the effects of influencing factors were further discussed.

1.3. Organization

The thesis starts with a literature review followed by experimental results focusing on the thermomechanical stability and fatigue behavior of Ni-Mn-Ga FSMA. It is continued with a theoretical analysis of the effect of SIM transformation on the crack tip SIF in order to understand the brittleness of Ni-Mn-Ga FSMA during thermal cycling.

- Chapter 2 describes the fundamental knowledge of MSM effect and recent developments in the Ni-Mn-Ga FSMAs. The thermally induced fatigue behaviors in SMAs are also briefly reviewed in this part.
- Chapter 3 describes experimental procedures and presents the results of material properties characterization of Ni-Mn-Ga single crystals. It includes the phase transformation temperatures, shape memory strain, magnetic properties, and magnetomechanical behaviors, etc.
- In Chapter 4, the thermomechanical stability of TWME under thermal cycling is presented with a focus on the cause of irregularity in the TWME and the influencing factors.
- In Chapter 5, microscopic observations are presented to understand crack initiation and propagation behaviors during thermal cycling. Different crack propagating modes are noticed and the failure mechanisms are suggested.
- In Chapter 6, the effect of localized SIM transformation, as a result of stress concentration around the crack tip, on the crack tip SIF is theoretically analyzed through redistributing the local stresses.

Results of the above work are summarized in the last chapter.

Chapter 2 Literatures review

The MSM effect was discovered by Ullakko et al. in 1996 [4, 5] on a unstressed Ni-Mn-Ga single crystal. A magnetic field induced strain (MFIS) of 0.2% was produced along the $[001]_c$ direction under the magnetic field of 8 kOe at the temperature of -8°C . Since then, plenty attentions have attracted and research works were carried to understand the MSM effect as well as the material properties of the Ni-Mn-Ga FSMA. Much larger MFIS up to 6%, 9.5% and 13.5% had been obtained more recently in Ni-Mn-Ga with different crystal structures, respectively [6, 7, 53]. The progresses are briefly reviewed in this chapter.

2.1. Introduction

2.1.1. Shape memory and twin boundary motion

Generally, shape memory effect (SME) is strongly related to the phase transformations between high temperature phase (austenite) and low temperature phase (martensite), especially the martensitic one. This first-order phase transformation allows the martensite to grow in the austenite without creating long-range stress fields or excess interfacial energy (no atomic migration is required) [54]. Thus, the shape recovery can be obtained with the reversal transformation by structural reconstruction. There are four characteristic temperatures defining the thermoelastic phase transformations. One is the martensite start temperature, M_s , at which martensite first appears in the austenite. The transformation proceeds with further cooling and is complete at the martensite finish temperature, M_f . Below M_f , the entire body is in the martensitic phase and typically consists of many

regions each containing a different martensite variant. During heating, the austenite start temperature, A_s , is the temperature at which austenite first appears in the martensite. With further heating, more and more of the body transforms back to austenite, and this reverse transformation completes at the austenite finish temperature, A_f . Above A_f , the specimen is in the original undistorted state. Occasionally, $T_m = (M_s + M_f)/2$ and $T_a = (A_s + A_f)/2$ are used to denote the martensitic and austenitic transformation temperatures, respectively.

Assuming single crystal SMA is cooled from the parent phase to a temperature below T_m , martensite variants forms in a self-accommodating manner to minimize the elastic energy. During this process, the shape of the specimen has not changed macroscopically, but there are twin-related martensite variants in the body and the boundaries between the corresponding twin variants are quite mobile. If an external load is applied, the twin boundaries need to move to accommodate it and deformation consequently occurs. When the stress is high enough, the martensite will become a single variant which is stable under the stress. Now, with the specimen heated to a temperature above T_a , reverse transformation happens and if this transformation is crystallographically reversible, the original shape is regained after $T > A_f$. It is worth noted that the multiple martensite variants formed within a single crystal are crystallographically equivalent but the orientations are different, resulting in a strain incompatibility at the variant boundaries. To minimize strain energy without loss of coherence at the variant boundaries (i.e. without degradation by fracture), the variants have to be deformed. The multi-variant state can be transformed into a nearly single variant of martensitic phase by appropriate mechanical treatment. Such a complete process is illustrated in Fig 2.1a. Simultaneously, the physical properties, such as dimension, electrical resistance, and etc. will be changed due to the

accommodated crystal deformation (Fig. 2.1b). The transformation temperatures can be determined consequently.

Figure 2.1. (a) Primary mechanism of the shape memory effect under load and heating cycle [55] and (b) hypothetical plot of properties change as a function of temperature for a phase transformation in SMAs.

There is another unique property in the SMAs named superelasticity. SMA exhibits pseudoelastic behavior because of the stress-induced martensitic (SIM) and its reverse transformations when a proper uniaxial stress is applied to a specimen and released above A_f . The stress-induced martensite is stable under stress, but is unstable in the absence of

stress, at temperature above A_f . Details of this phenomenon and its applications are systematically introduced in [55, 56].

In the SMAs, martensite grows or shrinks pseudoelastically responding to the stimulus, for example a change in the load, to maintain a certain balance between the mechanical and elastic energies. Analogy to the mechanism, the MSM effect is expected to present if the magnetic-field-induced stress can replace the mechanical one. The reasonability is that independent on the physical nature, the same driving forces (magnetic or mechanical) applied to the twin boundaries should produce the same macroscopic deformation. In the Ni-Mn-Ga FSMA, rearrangement of the martensite variants under an magnetic field has already observed by optical microscopy [57, 58]. High-speed videos [57, 59] taken during the magnetic field actuation confirmed that upon the application of a transverse field, twin variants magnetizing parallel to the field appeared and grew, causing the sample to extend vertically against the applied mechanical stress. Therefore, it is worth pointing out that strictly speaking, the MSM effect occurs only in the martensitic states. However, field-induced martensite transformation at the temperature above A_f aided by the mechanical stresses (80~100 MPa), similar to the superelasticity phenomenon in conventional SMAs, was also termed as the MSM effect in some literatures [60-62].

It is often noticed that intermartensitic (or premartensitic) transformations present before the appearance of austenite in the Ni-Mn-Ga FSMA [63-68]. Internal mechanical stresses are necessary for the onset of the intermartensitic transformation [68-70]. More details are described in Section 2.2.

2.1.2. Ferromagnetism

Ferromagnetic materials can be strongly magnetized in the field direction so that they have a rather high magnetic susceptibility (χ) [71], a ratio of magnetization to the applied magnetic field. At low temperature ($T < T_c$), the magnetization increases up to the saturation value with increasing the field strength. However, if the material is heated up to higher than its Curie temperature (T_c), the ferromagnetic state is unstable and the magnetic dipole moments are redistributed towards random orientations. It is the so-called ferromagnetic-paramagnetic transition, accompanied with a sharp drop of magnetization as well as the magnetic susceptibility, as illustrated in Fig. 2.2a. Consequently, the Curie temperature can be determined from measuring the ac low-field magnetic susceptibility directly, or from the relationship between magnetization and temperature under a constant field by using the superconducting quantum interference device (SQUID) [65, 72, 73]. Fig. 2.2b shows that the effect of temperature on the magnetization is relied on the field strength, though all the curves show change in the magnetization at the transformation temperature. It is reasonable that magnetization increases in stronger magnetic fields. The influence of paramagnetic-ferromagnetic transition on the crystal structure is negligible that the structure does not distort on entering the ferromagnetic phase [74, 75].

Figure 2.2. (a) Low-field magnetic susceptibility χ and constant field (1 T) magnetization of a $\text{Ni}_{48}\text{Mn}_{31}\text{Ga}_{21}$ single crystal as a function of temperature [72]; (b) magnetization as a function of temperature at different field strengths [63].

At a certain temperature below M_f , the magnetization versus magnetic field curves are dependent on the martensite structure, relative proportion of martensite variants, their respective easy and hard axis orientations, etc [76]. The overall magnetization is a superposition of magnetization of all the martensite variants. But for a given specimen at constant temperature, magnetization saturation value is the same in all the crystallographic directions. Before saturation, the magnetization depends not only on the field strength but also on the crystallographic direction along which the magnetic field is applied, which is termed magnetocrystalline anisotropy. Local crystallographic structure determines the easy axis of magnetization in the absence of a magnetic field. For Ni-Mn-Ga martensites, the easy axis is always along the shortest crystallographic axis (c axis) [7, 77-79]. When an external magnetic field is applied, the local magnetic moments are aligned.

Magnetocrystalline anisotropy energy, the energy cost per atom (unit volume) to align its magnetization from one crystallographic direction to another, is introduced to characterize

the dependence of magnetic properties on the crystallographic direction [80]. The magnetic anisotropy energy (MAE) density K is exactly equal to the magnetic driving force applied to the twin boundary [57, 81]. It is one of the most important material properties of FSMA with respect to the MSM effect. High MAE of the martensites provides large magnetic stresses on the twin boundary between differentially oriented twin variants. For the Ni-Mn-Ga alloys, their tetragonal martensite is magnetically uniaxial, and the expression for the local anisotropy is described by means of [71, 82, 83],

$$\phi_K(\mathbf{r}) = K_1(\mathbf{r}) \sin^2 \varphi(\mathbf{r}) + K_2(\mathbf{r}) \sin^4 \varphi(\mathbf{r}) + \dots \quad (2.1)$$

where K_1 and K_2 are the first and second anisotropy constants and φ is the angle between the magnetization $\mathbf{M}$ and magnetic field axis. The main source of MAE is the spin-orbit coupling, so that it can be calculated via the density-function theory as a difference in the total energy between the different magnetization directions [84].

The magnetic anisotropy of Ni-Mn-Ga alloys in the parent phase is rather low, in the order of 10^3 J/m^3 , and it is two orders higher in martensite [6, 9, 76, 85, 86]. The magnetic anisotropy constants in the martensite is a function of temperature, decreasing more and more steeply with increasing the temperature [77, 78, 87, 88], as shown in Fig. 2.3. For example, the first magnetic anisotropy constants of a $\text{Ni}_{48.9}\text{Mn}_{27.7}\text{Ga}_{23.4}$ martensite with $5M$ structure are $2.65 \times 10^5 \text{ J/m}^3$ and $2.0 \times 10^5 \text{ J/m}^3$ at 130 K and 283 K, respectively [77], while the second anisotropy constant is negligible, less than 4% of the first ones. At room temperature, the magnetic anisotropies values are mainly determined by the martensite structures, so they are also influenced by the chemical composition [76, 78, 88, 89]. For example, the anisotropy constants of a $5M$ tetragonal martensite ($\text{Ni}_{49.7}\text{Mn}_{29.1}\text{Ga}_{21.2}$) is $K_1 = 1.65 \times 10^5 \text{ J/m}^3$ and K_2 negligible, while those of $7M$ orthorhombic martensite

($\text{Ni}_{50.5}\text{Mn}_{29.4}\text{Ga}_{20.1}$) are $K_1 = 1.7 \times 10^5 \text{ J/m}^3$ and $K_2 = 0.9 \times 10^5 \text{ J/m}^3$, and $K_1 = 2.3 \times 10^5 \text{ J/m}^3$ and $K_2 = 0.55 \times 10^5 \text{ J/m}^3$ for the *NM* tetragonal martensite ($\text{Ni}_{50.5}\text{Mn}_{30.4}\text{Ga}_{19.1}$), respectively. The crystal structure terms, *5M*, *7M* and *NM*, will be explained in section 2.2. Experimentally, the magnetic anisotropy can be determined from the magnetization curves [38, 90].

Figure 2.3. Temperature dependence of the magnetic anisotropy and of the saturation magnetization [77]; the inset shows the magnetization curve measured both along the [100] and the [001] directions at 143 K.

Microscopic magnetic domains exist in martensite variants so that the magnetic dipole energy can be reduced. The magnetic domains in Ni-Mn-Ga alloys have been investigated by scanning electron microscopy (SEM, Type II contrast) [91-93] using the backscattered electron mode with bitter pattern imaging, magnetic force microscopy (MFM) [43], and transmission electron microscopy (TEM) [94-97] with Lorentz microscopy and electron holography. Different magnetic domain structures have been observed [91, 92, 94, 97]. Both parent and martensitic phases show mainly stripe domain structures with long 180° walls (Fig. 2.4). However, diamond-shaped and Labyrinth domains are also found when the magnetization axis is out of plane. The magnetic domains in the parent phase have a

size ranging from 10^2 to 10^4 nm, and are subdivides into finer pieces ($<10^2$ nm) in the martensite. The magnetization distribution in the parent phase can be inherited to the intermartensitic phase, but is dramatically modified by the transformation to the tetragonal martensite [97]. During the forward transformation, the magnetization rotation does not necessarily occur at the same time as the martensite variants grow [94]. In martensite, the easy axes change the directions as they traverse from one twin variant to another, exhibiting peculiar zig-zag lines [95, 98], which is a characteristic feature of the martensite with multiple variants. Some early models [99, 100] had considered each twin band in the martensite has a single magnetic domain. But experimental results [95] show that each twin variant is divided into several small magnetic domains while the twin variant boundaries also correspond to magnetic domain walls.

Figure 2.4. The stripe magnetic domains run along the a -axis under SEM observation with the type II magnetic contrast [93]

In the vicinity of martensitic transformation, the application of a magnetic field will induce a large change of entropy, indicated by a considerable magnetization jump caused by the structure transformation [101]. This magnetic entropy change $\Delta S(T, H)$ is defined from the Maxwell relations for a system with first-order transition as [102]

$$\Delta S(T, H) = S(T, H) - S(T, 0) = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH \quad (2.2)$$

which is a function of the temperature and applied magnetic field [103-106]. The magnetic entropy change provides a potential usage of Ni-Mn-Ga FSMA as the magnetic refrigerants materials.

2.1.3. Magnetic shape memory effect

Large MFIS is realized through twin variants reorientation by the movement of highly mobile twin boundaries [4, 5, 9, 57]. When an appropriate magnetic field is applied to the sample with a large enough MAE, it will be energetically favorable to redistribute the twin variants inside the body. Instead of rotating the magnetization with respect to their local crystal structure, the twin variant boundaries move to align the easy axes along with the field direction, leading to a large shape change. The deformation mechanism is supported by the direct observation on the twin boundary motion with progressively increasing field [98], and simultaneous measurements of magnetization and strain as a function of magnetic field [65, 77]. Fig. 2.5 is a schematic diagram comparing this mechanism to those of the thermally active SME and magnetostriction.

Consequently, a very low twinning stress is crucial for the MSM effect to occur [100]. The high mobility of martensite variant boundaries were confirmed in an internal friction study [107]. The critical detwinning stresses are 1~4.5 MPa for Ni-Mn-Ga FSMA with the *5M* and *7M* structures [7, 81, 108-113], but are larger (12~20 MPa) for those with the *NM* structure. The exact values are also affected by the testing temperature, chemical compositions, and so on.

Figure 2.5. Deformation mechanisms of the traditional magnetostrictive, thermally active SME and MSM effect (For simplicity, twin variants are assumed to consist of single magnetic domain and the favorable orientation of magnetization $\vec{M}$ is parallel to $\vec{H}$).

From the macroscopic point of view, the criterion of MSM effect is that the difference in MAE (ΔE_{mag}) exceeds the (elastic) energy needed to move the twin boundaries [4, 34, 37, 42, 81, 114, 115]. Assuming at a given temperature T , the specimen is magnetization saturated along the easy axis of one martensite variant but perpendicular to that of the adjacent variant, the MSM effect occurs in the free stress condition when

$$\Delta E_{mag} > \varepsilon_0(T) \cdot \sigma_{tw}(T, \varepsilon) \quad (2.3);$$

and if there is a external stress (σ_{ext}) applied in the direction perpendicular to the magnetic field direction,

$$\Delta E_{mag} \geq \varepsilon_0(T) [\sigma_{tw}(T, \varepsilon) + (\sigma_{ext})] \quad (2.4);$$

where $\varepsilon_0 = 1 - c/a$ is the tetragonal distortion and σ_{tw} is the twinning stress (mechanical stress necessary for twin variant rearrangement). Consequently, the condition of obtain a reversible strain on the reverse path is deduced in the form

$$\Delta E / \varepsilon_0 - \sigma_{tw} > \sigma_{ext} > \sigma_{tw} \quad (2.5);$$

To observe a reversible MFIS, ΔE_{mag} needs to be smaller than $\varepsilon_0 \sigma_{TW}$, and the condition $2\sigma_{TW} < K_u/\varepsilon_0$ should be satisfied to have a fully reversible strain [116].

Single variant signification is expected to obtain a larger MFIS. Mechanical treatment, such as applying a constant stress (3~14 MPa), for example, on the [001] direction, at constant temperature ($< M_s$) can be adopted [79, 117, 118]. It seems that cooling the specimen from high temperature down to martensite under loads [62, 77, 92, 119-121] or the magnetic field [43, 104, 122] is more effective. The magnetic/mechanical stress changes the preferential orientation of the martensite variants during cooling [123, 124].

It is summarized that occurrence of the MSM effect needs the following conditions:

- The martensitic phase possesses a large magnetocrystalline anisotropy;
- Very low detwinning stress (~ 1 MPa);
- Strictly speaking, the temperature is below T_m and T_c ;
- Single crystal configuration is preferred.

2.2. Crystal structure

The stoichiometric Ni_2MnGa compound was investigated by X-ray diffraction [125] and powder neutron diffraction [74, 126]. The results show that the parent phase is a body center cubic (BCC) structure with $\text{Fm}\bar{3}\text{m}$ space group ($L2_1$ Heusler atomic order), as showed in Fig. 2.6, with lattice parameter $a_0 = 0.5826$ nm. Martensitic transformation occurs at $T_M = 200$ K and the crystal structure is converted to a tetragonal structure with a

$= 0.5922$ nm and $c = 0.5566$ nm. For the off-stoichiometric alloys, the lattice parameters remain almost the same for the parent phase, but are changed with chemical composition and temperature in the martensitic state. It is necessary to point out that the lattice of martensite is slightly monoclinic, but the deviation of the angle γ from 90° is much small so that it is generally treated as tetragonal one [69, 75]. The deviation becomes smaller with decreasing T_m . About the martensite unit cell, some discussions are given in the appendix A.

Figure 2.6. Crystal structure of the Ni_2MnGa austenite: $a_0 = 0.5826$ nm, atomic positions are given as 1 Ga in (0, 0, 0), 3 Ga in (0, 1/2, 1/2), 3 Mn in (1/2, 0, 0), 1 Mn in (1/2, 1/2, 1/2), and 8 Ni in (1/4, 1/4, 1/4).

More precisely speaking, Ni-Mn-Ga martensite has a superlattice structure derived from the cubic Heusler structure by a periodic displacement of the atoms in successive (110) planes along the $[1-10]$ direction, or say $(110)[1-10]_c$ system (the subscript 'c' denotes the cubic phase) [69, 126]. They are characterized as five-layered (5M), seven layered (7M), and non-modulated (NM or T) modulated martensites, as well as some other unusual eight-layered (8M) and twelve-layered (12M) structures, respectively [69, 75, 127-131]. Types of layered structures can be distinguished by the extra spots on the electron diffraction patterns along the direction corresponding to the $(110)_c$ plane. X-ray diffraction (XRD),

selected area electron diffraction (SAED), and high resolution electron microscopy (HREM) observations [69, 128] suggested that the natures of $5M$, $7M$ and $10M$ are stacking of nearly close-packed planes with sequences $(3\bar{2})$, $(5\bar{2})$ and $(5\bar{5})$ in Zhdanov notation. The modulation may be shuffling or stacking of the basal planes, but the difference on the atomic positions according to these two models is practically hard to be distinguished. More details of the investigation on the microstructure are available in [46, 69, 128, 130, 132, 133]. Although it is not perfectly periodic, the HREM images reveal that the nature of layered structures is microtwinned, and each microtwin has a thickness of a few atomic planes [128].

Martensitic structures can be transited between each other by loading/unloading [132] or changing the temperature [65, 134]. At room temperature, the structures ($5M$, $7M$ and NM) are primarily dependent on the chemical composition [69, 131, 135-137]. The magnetic field has no effect on the modulation of the layered structures [125]. For a certain sample, the stability of structures, i.e. the order in which they appear, seems to be always the same. During cooling, the martensitic transformation evolution in the stress-free state includes the following sequences: $P \rightarrow 5M \rightarrow 7M$ ($\rightarrow 2M$) [68, 134] and $P \rightarrow 5M \rightarrow NM$ [65, 77]; here P denotes the parent phase. Reverse transformations $5M \rightarrow P$ or $7M \rightarrow P$ occur during the heating process. On the other hand, successive premartensitic transformations can be induced from the parent phase by increasing the mechanical loads at temperatures above T_m with the sequence of $P \rightarrow 5M \rightarrow 7M \rightarrow NM$ [132]. The mixture structure may consists of $5M$ and $7M$ phases or $7M$ and NM phases, but it was never observed as a combination of $5M$ and NM phases [75]. The crystal structure of martensite is an important factor that affects both the magnetic anisotropy and mechanical properties, and consequently influences the MSM behaviors.

For all the layered structures of Ni-Mn-Ga alloys, both lattice parameters and martensitic transformation temperature are dependent on the chemical composition, as well as the electronic valence concentration e/a [69, 75, 127, 129, 130, 137-139], as shown in Fig. 2.7. The electronic valence concentration is defined by $e/a = \text{at.\%Ni} \times 10(3d^8 4s^2) + \text{at.\%Mn} \times 7(3d^5 4s^2) + \text{at.\%Ga} \times 3(4s^2 4p^1)$.

- For $5M$ structure, the basic unit cell is approximate a tetragonal cell, though strictly speaking monoclinic with the angle between a and b axes $\gamma \approx 90.50^\circ$, with $c/a \sim 0.94$, $e/a = 7.55 \sim 7.7$, and T_m ranges from very low (< 77 K) to slightly higher than room temperature.
- For $7M$ phase, it is orthorhombic or monoclinic with $c/a \sim 0.89$; T_m is well above the room temperature but generally below T_c (340~390 K), and e/a in the range of 7.67~7.71;
- For NM structure, the unit cell is tetragonal with ratio $c/a > 1$ based on the x-ray diffraction data, e/a is from 7.61 to 7.82, and T_m in the wide temperature range of 323~550 K with $T_m > T_c$.

The thermal enthalpies of the martensitic transformation from $5M$ or $7M$ to austenite are similar but that from NM to austenite is higher [137, 140].

With e/a increases, the first martensitic structure to appear at room temperature is $5M$ followed by $7M$ and then NM structure [75, 88]. Fig. 2.7 shows that the boundary between different structures is not sharp and the approximate positions are 7.61 between $5M$ and $7M$, and 7.72 between $7M$ and NM structures. In the range from 7.61 to 7.72, different crystal structures ($5M$, $7M$, or NM) are observed.

Figure 2.7. Lattice parameters ratio c/a at $T = 298$ K as a function of T_m and e/a , respectively, for the alloys with $5M$, $7M$ and NM structures [75]. The dot-line boundaries define the region in which all the phases were observed.

The maximal obtainable MFIS value is limited by the lattice parameters of the martensite unit cell, namely $|1 - c/a|$. They had been obtained experimentally in $5M$ and $7M$ structures [6, 7], but not observed so far in the NM structure, with the lattice tetragonality approaching the maximum $c/a \approx 1.23$ [53, 75], despite the high magnetic anisotropy [141]. It may be due to the high twinning stress, 12~20 MPa, for the NM structure [127, 142-144]. Comparing, much lower compressive stresses (1~3 MPa) are critical for $5M$ and $7M$ structures to reorient the twin variants [7, 57, 112, 116, 119, 141].

2.3. Influencing factors

Many factors may affect the MSM behaviors of the Ni-Mn-Ga FSMA, such as the chemical composition, temperature, magnetic field strength, constrain, crystal orientation, etc. Some of these factors are strongly interdependent. In this section, the variables which illustrate the physical basis of the MSM effect are given the major attention.

2.3.1. Composition and electron concentration

It is found that M_s and the premartensitic transformation temperature T_l [66, 137, 145-149], transformation heat [147, 150], Curie temperature T_c [140, 151, 152], lattice parameters ratio at room temperature (c/a) [75, 151], and the magnetic properties [75, 88, 89, 108, 150, 153] are determined or strongly affected by the alloying composition, or more precisely, the valence electron concentration. A general view of the transformation temperature shift as a function of element contents is summarized in [146, 147]:

- At a constant value of Mn content, Ga addition lowers M_s temperature;
- Mn addition (instead of Ga) at constant Ni concentration causes M_s decrease, coincided with the result in [148] but opposite to the results in [140] (Mn increase, M_s increase);
- Substitution of Ni atoms by Mn at constant Ga contents results in alloys with lower M_s , also confirmed in [149].

Further investigations indicate that there is a linear relationship between e/a and M_s [66, 147, 150], or between c/a and T_m [75]. For example, equations are given in [150],

$$T_m = 702.5 \times (e/a) - 5067 \quad (2.6a)$$

or
$$T_m = 1960 - 21.1 \times \text{Mn(at.\%)} - 49.2 \times \text{Ga(at.\%)} \quad (2.6b)$$

which is applicable in the range of Mn: 20-35at.% and Ga: 18-27at.%. The linear relationship may be related to the Hume - Rothery mechanism [138]. From the practical point of view, the transformation temperatures are expected to be higher than room temperature to avoid the unnecessary cooling of the device.

The Curie temperature decreases with increasing Ni content [151, 153] or increasing Mn content at constant Ni content [140]. However, the change in T_c with composition deviation is less significant and the temperature range is relatively narrow (340~390 K) [154]. Some fourth elements can influence T_c more effectively [138, 154-159]: T_c increases when Ni is substituted by either Fe or Co, and decreases with the substitution of Mn for V or Ga.

Figure 2.8. An empirical composition map for designing Ni-Mn-Ga FSMA. The shaded area indicates the compositions with $T_c > M_s > 300$ K and magnetization saturation value $M_s > 60$ emu/gm [150].

As for the magnetic properties, the effects of chemical composition on the magnetic anisotropy constant are briefly mentioned in sec. 2.1.2. Besides, the magnetic anisotropy of 5M structure increases with increasing Mn content [75, 84] and the saturation magnetization is a function of e/a , decreasing linearly from the peak at stoichiometry ($e/a = 7.5$) regardless of the martensitic structure [160].

2.3.2. Magnetic field

When Ni-Mn-Ga alloys with $5M$ or $7M$ structure ($c < a$) is exposed to the magnetic field, it contracts along the field direction since the easy direction is also the c -axis of martensite. A reversible MFIS can be achieved through rotation of magnetic field, which drives the martensite twin boundaries back and forth via switching the crystal lattice [109, 116, 161]. The shape change remains if the magnetic field is removed. If a constant magnetic field is applied, totally recoverable strain can be obtained by loading and unloading the mechanical stress [109, 116]. The twinning stresses increase with increasing the magnetic field strength [161, 162].

Martensitic transformation temperature T_m shifts when a magnetic field is applied during cooling. It is explained as a result of the anisotropic magnetoelastic interactions in the ferromagnetic martensitic phase, or say the magnetic field induced mechanical stresses [68, 163]. There is a large change in magnetic moment associated with the thermoelastic martensitic transformation [4, 63]. Theoretically, the dependence can be calculated by an modified Clapeiron-Clausius approach [60, 164, 165]:

$$\frac{dT}{dH} = \frac{\Delta M}{\Delta S} \quad (2.7)$$

where ΔS is the entropy change, and ΔM the magnetization change. However, in the literatures, the calculated values of $\Delta T/\Delta H$ ranges from 0.02 to 0.6 K/kOe among the Ni-Mn-Ga alloys with different chemical composition [60, 149, 166-169]. Thus, the influence of magnetic field on the T_m temperature shift was considered complex. Recently, systematical investigations [68, 170] show that the slope varies with the phase transformations with different sequences ($P \rightarrow 5M \rightarrow 7M \rightarrow NM$). The effect of magnetic

field on T_m disappears when the field is removed [149, 165]. The premartensitic transformation temperature T_I decreases almost inversely proportionally with increasing the magnetic field [63, 171], and stops changing when the magnetic field reaches high enough, for example, 2T [125, 172]. Temperature hysteresis of the phase transformation was reported independent on the field strength in a $\text{Ni}_{2+x-y}\text{Mn}_{1-x}\text{Fe}_y\text{Ga}$ ($x = 0.19$, $y = 0.04$) alloy [168, 173], but more recent experiments on a $\text{Ni}_{2.18}\text{Mn}_{0.82}\text{Ga}$ alloy show that it decrease with increasing the magnetic field [174].

2.3.3. Temperature

Magnetization of Ni-Mn-Ga FSMA is dependent on the magnetic field as well as temperature. Fig. 2.9 shows typical magnetization curves in the condition of varying the field strength while keeping the temperature constant, and vice versa [63, 73, 77, 174-176]. In isothermal magnetization measurement, the general shape of magnetization curve, switching field (the critical magnetic field necessary to activate twin boundary motion), and magnetization saturation are all influenced by the temperature. On the other hand, magnetization curves with changing the temperature covering the phase transformation under constant magnetic field show anomalies at both the temperatures T_m and T_I . It implies that the structural transition affects the magnetic moment distribution. The differences in the magnetization versus temperature curves are theoretically explained in [176], resulting from the difference among M_s , T_c in the parent (T_{ca}) and in the martensitic (T_{cm}) phase. With decreasing temperature, the magnetic anisotropy K increases at first but saturates finally [78, 79, 87, 89, 177-180]. For the uniaxial anisotropy of the martensite with $5M$ structure, the temperature dependence of $K_I(T)$ far below T_c follows the third power of magnetization [181].

$$K_I(T)/K_I(0) = [M_s(T)/M_s(0)]^3 \quad (2.8)$$

For $7M$ and NM structures, the temperature dependence of K_I and K_2 follows the similar power law but the exponent n is rather between 2 and 3.

Figure 2.9. (a) Typical magnetization curves of a $\text{Ni}_{48.5}\text{Mn}_{30.3}\text{Ga}_{21.2}$ single crystal at different temperatures [175]: (A) austenite, (B) $5M$ structure (the magnetization jump is a result of twin variant reorientation), and (C) NM structure. (b) Magnetization of a $\text{Ni}_{52}\text{Mn}_{24.4}\text{Ga}_{23.6}$ single crystal as a function of temperature under different magnetic field [77].

MFIS and lattice deformation increase approximately linearly with increasing the temperature (below M_f), and approach the maximum at the temperature closest to T_m [65, 67, 72, 75, 87, 179, 180], as shown in Fig. 2.10. Meanwhile, the switching field falls with increasing temperature due to the increased twin boundary mobility. The relationship between twinning stress and temperature has an exponential-like character [62, 110, 143]. For example, Fig. 2.10c [87] shows that the twinning stress increases exponentially with decreasing the temperature. There is a temperature limitation out of which no MSM effect occurs. The temperature limitation is related to the relationship between the magnetic energy and the elastic energy necessary to move the twin boundaries [72, 182].

Figure 2.10. The effects of temperature on the MSM properties for non-stoichiometric $\text{Ni}_{49}\text{Mn}_{29.6}\text{Ga}_{21.4}$ alloy with $A_s = 310.7\text{ K}$ and $M_f = 302.8\text{ K}$: (a) the strain measured along the $[001]_c$ direction, (b) The tetragonality as a linear function of temperature in the range of 297–310 K [179] and (c) The occurrence of MSM effect is limited by T_a and the point where the magnetic stress is less than the critical twinning stress [87].

2.3.4. Mechanical Load

Mechanical load is often used to balance the magnetic field induced stress to obtain a recoverable MFIS [6, 81, 110, 183-186]. When the field direction is perpendicular to the mechanical stress, mobile planes are formed to separate the two parts which are favored to the magnetic and mechanical fields, respectively, as shown in Fig. 2.11. With certain mechanical stress of 1~2 MPa, it is beneficial to obtain the maximum reversible strain in actuation because the MSM material can be brought back to the initial state when the

magnetic field is removed. MFIS decreases with increasing mechanical stress, and it is totally suppressed if the mechanical stress is strong enough. One example of the stress dependence of MFIS is illustrated in [85]. On the other hand, larger mechanical stress demands a stronger magnetic field for the MFIS to saturate.

Figure 2.11. Schematic of martensite variants rearrangement under magnetic field and mechanical stress. The specimen is supposed to consist of a single twin system. Strains are induced through twin boundaries motion.

Stress-induced variant rearrangement will cause the change in magnetization [85, 187, 188]. There are only three different variants and consequently only three directions of the easy axis approximately normal to each other. The magnetization curve of a twin-related martensite with arbitrary twin distribution will be a superposition of magnetization curves of variants with different crystal orientations

$$M(H) = \phi M_{ea}(H) + (1 - \phi)M_h(H) \quad (2.9)$$

Where ϕ is the fraction of the variants with easy axis in the field direction, M_{ea} and M_h are the magnetization of variants with easy and hard magnetic axes in the field direction, respectively.

The dependence of the transformation temperatures on the applied mechanical loading can be predicted in the framework of the Clausius-Capeyron equation, e.g. hydrostatic:

$$dT/dp = T_0(V_A - V_M)/V_A q m \quad (2.10a);$$

and uniaxial (the one-dimensional analog):

$$d\sigma/dT = -q(\sigma)m/T_0(\sigma)\varepsilon \quad (2.10b).$$

The relationship between hydrostatic pressure p (uniaxial compression stress σ) and transformation equilibrium temperature T_0 depends on the transformation latent heat, q transformation volume change $(V_A - V_M)/V_M$ (transformation strain ε in the direction of applied stress σ) and mass density m , respectively. Application of hydrostatic pressure to the stoichiometric Ni-Mn-Ga results in a increase in T_m with the rate $dT_m/dP = 5.5$ K/GPa [189, 190], while T_m increase at much faster rates ($dT_m/dP = 1.5\sim 4$ K/MPa) when the stress is uniaxial (compressive) [129, 191, 192]. A stress-temperature phase diagram (Fig. 2.12) is drawn for specific chemical composition [62, 190] to indicate the sequence of stress-induced transformations. Based on it, the thermodynamic properties, such as the transformation temperatures and latent heat, can be deduced.

Figure 2.12. σ -T phase diagram of $\text{Ni}_{52}\text{Mn}_{24.4}\text{Ga}_{23.6}$ single crystal under compression along the $\langle 110 \rangle_P$ axis [62]. Solid and dotted lines correspond to linear regression fits of the forward and reverse transformation data.

There are still some other influencing factors. For example, mechanical deformation history has a strong influence on the critical twinning stress and strain due to the internal stress field [193]. Besides, the MFIS decreases with increasing the frequency during cyclic deformations [194]. Heat treatments can also influence the thermal and physical properties of the Ni-Mn-Ga FSMA [195-198]. Ageing, both at the parent or martensitic phases, affects the transformation temperatures though the difference depends on the chemical composition. It is attributed to the improvement of the degree of atomic orders. Austenite aging can also increase the Curie temperature and magnetization. Annealing increases the Curie and martensitic temperatures, as well as the saturation magnetization.

2.4. Models on the MSM effect

To explain the origin of MSM effect and related phenomena, several models have been proposed to describe the magnetic-field-induced strain/stress in Ni-Mn-Ga FSMA, which

are reviews elaborately in [119, 199]. Here, a brief description will be given without procedural details but with some discussion on the applicability.

Ullakko [5, 200] gave the first explanation of MSM effect based on the field-induced reorientation of twin variants. Given the effect of magnetic field equals to an mechanical stress, in the case of two-variant geometry (Fig. 2.13), the magnetic field induced stress acting on the twin boundaries is [57, 100, 119]

$$\sigma_{mag}(\mathbf{h}) = \varepsilon_0^{-1} \int_0^h (\mathbf{m}_a(\mathbf{h}) - \mathbf{m}_t(\mathbf{h})) d\mathbf{h} \quad (2.11)$$

where $\mathbf{m}_a(\mathbf{h})$ and $\mathbf{m}_t(\mathbf{h})$ denote specific magnetization values per unit volume for both twin variants. The magnetic stress becomes independent on the field strength in strong fields, approaching its saturation value $\sigma_{mag}(\mathbf{h}) \xrightarrow{h \rightarrow \infty} K_u / \varepsilon_0$. Assuming a general balance equation between the mechanical and magnetic stresses $\sigma_{mech}(\varepsilon) = \sigma_{mag}(\mathbf{h})$, the magnetic-field-induced strain is

$$\varepsilon_{mag}(\mathbf{h}) = \varepsilon_{mec}(\sigma_{mag}(\mathbf{h})) \quad (2.12)$$

A Fermi-like distribution function was adopted to approximate the mechanical stress-strain curve [57],

$$\varepsilon_{mec} = \varepsilon_0 \left(1 + \exp \left(\frac{\pm \sigma_0 - \sigma}{\Delta \sigma} \right) \right)^{-1} \quad (2.13)$$

where ε_{mec} is the strain from the mechanical stress-strain curve, σ is the stress along the $[001]_c$ direction, σ_0 and $\Delta \sigma$ are the characteristic stress parameters as defined by $\sigma_s = \sigma_0 - 2\Delta \sigma$ and $\sigma_f = \sigma_0 + 2\Delta \sigma$, where σ_s and σ_f are the start and finish twinning stresses, respectively. This model provides quantitative prediction of the magnetization

and MFIS. However, it needs experimental results to support the prediction which weaken its effectiveness.

Figure 2.13. two-variants twin microstructure, easy axis alignment and magnetic driving force responsible for twin boundary motion in an applied magnetic field [57].

James and Wuttig [80, 201] gave a numerical prediction of MFIS, as well as images of the twin variant rearrangements. Such micromagnetic model is a structural optimization to obtain the energy minimization of Zeeman, MAE, magnetostatic, and mechanical energies of the Ni-Mn-Ga single crystal, among which there are multiple but competing interactions. Therefore, only certain twin systems are allowed to exist in the crystal structural and a finite set of deformation is possible. However, the difficulty is to obtain the complex crystal structure in advance, and the predicted MFIS is much smaller, not in the same order with the experimental results.

O'Handley [114] pointed out that the maximum strain output is proportional to the Zeeman energy $M_s H$. Models [44, 202] continued to describe the twin boundaries movement under both loads and magnetic field. The primary result is that when either mechanical or magnetic energy becomes larger than the other, the twins will move to

abruptly rearrange the entire sample to a variant stable under the new condition. The maximum strain achieved in a given field will decrease as the twinning strain increases because of the increase in the elastic restoring force. If the volume consists of 100% certain variant when strain equals to zero, the MFIS is expressed as [184, 203],

$$\varepsilon(H_{nd}) = \varepsilon_0 \left(\frac{2K_u H_{nd} (1 - H_{nd}/2) - \sigma \varepsilon_0}{C_{eff} \varepsilon_0^2} + \frac{1}{2} \right) \quad (2.14)$$

where ε_0 is the crystallographic strain limit, σ is the applied stress, C_{eff} is the elastic modulus of the twinned state, K_u is the magnetic anisotropy, $H_{nd} = M_{sat}H/2K_u$ is the non-dimensional magnetic field, M_{sat} is the saturation magnetization and H is the applied magnetic field. An analytical model [204] was given to predict the field-induced strain achievable in ensembles of particles having specified orientations distributions.

Phenomenological models [205, 206] of the Helmholtz free energy are used to derive the expressions of static magnetic susceptibility, field induced strain, and magnetization for the martensite. In this framework, the equilibrium states of a multi-variant microstructure is calculated [207], predicting the decrease in saturation strain with increasing the mechanical stress. The drastic magnetization changes occurring in the vicinity of the martensitic phase transition are predicted, and the deduced temperature dependence of magnetization is satisfied with the experimental results. However, twin boundary motion is not included in this approach so that the calculated MFIS is rather underestimated.

Attempts were proposed to describe the magneto-mechanical coupling giving rise to magnetoplasticity on the microscopic scale in [208, 209]. The main postulation is that the deformation is carried by twinning dislocations located in steps of twin boundaries [210,

211]. It is the competing between magnetic and mechanical forces push the twin dislocation to move (Fig. 2.14). The following deductions are based on previous understanding of the twinning dislocation [212-214]. As a result, the magnetostress τ_{Mag} , which is defined as the shear stress on the twinning plane in the direction of the Burgers vector $\mathbf{b}$ of the twin dislocation, is calculated [215],

$$\tau_{Mag} = \frac{F_{Mag}}{s} = \begin{cases} \frac{\mu_0 \mathbf{M} \mathbf{H}}{s} (1 - \frac{\mu_0 \mathbf{M} \mathbf{H}}{4K}) & \mathbf{H} \leq \mathbf{H}_A \\ K/s & \mathbf{H} \geq \mathbf{H}_A \end{cases} \quad (2.15)$$

where F_{mag} is the magnetic force, s the twinning shear $s = d/b$, H_A the switching field, K is the magneto anisotropy, and μ_0 , $\mathbf{M}$ and $\mathbf{H}$ are as usual. The twin variant is magnetic favored when $\tau_{Mag} > \tau_{Mech}$, and the twin variant is mechanical favored vice versa. The predicted stress is coincided with the experimental results [109]. But it is unsure for a prediction to use the concept “twin dislocation”, which is still ‘under the amplifier’ and the properties are not clear so far.

Figure 2.14. The competition between mechanical and magnetic stress applied on the twin dislocation

2.5. Some other aspects

It is necessary to tell the difference between ‘magnetic field induced stress’ and ‘magnetostress’ because these terms are not used properly in some literatures. Magnetic field induced stress [57, 216-218] is a macroscopic parameter, and can be calculated from the magnetic anisotropy and magnetic field induced strain (Eq. 2.11). Experimentally, it can be measured according to the following equation, as indicated in Fig. 2.15a,

$$\sigma_{mag}(H, \varepsilon) = \sigma_{mech}(H, \varepsilon) - \sigma_{mech}(0, \varepsilon) \quad (2.16).$$

Its magnitude is a linear function of H at small magnetic field and saturates at strong field (Fig. 2.15b), similar to the field dependence of magnetization [112, 217]. Comparatively, magnetostress [109, 215] is introduced as a internal shear stress on the twinning plane, as defined by Eq. 2.15. Its magnitude has a similar dependence on the magnetic field strength with respect to that of the magnetic field induced stress. What’s more, twinning stress is an internal parameter depending on the crystal structure and its state, e.g. thermomechanical history, loading mode and applied stress direction [110]. Experimentally, this parameter should be determined from the plateau in the stress vs. strain curve [188].

Figure 2.15. (a) The increase in the detwinning stress with applying a magnetic field of 0.55 T by comparing the stress-strain curves along [100] direction of a $\text{Ni}_{48.8}\text{Mn}_{29.7}\text{Ga}_{21.5}$ single-variant sample at 293 K; (b) Field dependence of the increase in twinning stress. Both are cited from [112].

For the microelectromechanical systems (MEMS) application, fabrication of the Ni-Mn-Ga thin films is expected. The thin films have been grown by molecular beam epitaxy (MBE) [219-221], R.F. magnetron sputtering [222-224], ion-beam sputtering [225], and pulsed laser deposition [226-229] on different types of substrates. The thickness of as-deposited thin film ranges from ~30 nm to 5 μm . Comparing to the bulk material with the same chemical composition, the material properties of the thin films, such as the transformation temperatures, Curie temperature and magnetocrystalline anisotropy, are slightly changed. Partial crystallization is possible in the thick thin films, and it can be compensated by increasing the substrate temperature or heat-treatment (annealing) of the as-deposited thin films. MSM effect and TWME have been observed within certain thin films in the free-standing state, independent of the deposition method. The Ni-Mn-Ga thin films exhibit better ductility than the polycrystalline bulk specimens [230, 231].

As for the applications, Ni-Mn-Ga alloys exhibiting the MSM effect have been used to produce actuators [40, 232]. The generated force can be up to 2 kN, and a large stroke of 5 mm can be given, respectively, depending on the actuator construction. The coupling factor between magnetic field energy and mechanical work can be as high as 70%. They also have the potential to be used as a deformation sensor [233], energy absorption unit [234], magnetic refrigerants, and thin films can be used in MEMS, such as a optical microscanner [224].

2.6. Mechanical fatigue in SMAs

Fatigue, in simplified concept, is the accumulation of damage in the plastic zone at the crack tip from cyclic plastic deformation [235]. It accounts for the intrinsic mechanism of crack growth at the stress intensity factor (SIF, K) levels below the fracture toughness (K_{IC}), where $K/K_{IC} = 0.1 \sim 0.4$. Generally, the fatigue failure consists of several distinct processes involving initial cyclic damage, formation of an initial ‘fatal’ flaw (crack initiation), Stage I and II crack propagation (growth); and final catastrophic failure or instability. Comparing to most materials, the uniqueness in the fatigue properties of SMAs is that a much longer fatigue life ($10^5 \sim 10^7$) can be obtained with large cyclic deformation (strain $> 2\%$). A brief review on the SMAs fatigue, which refers to mechanical fatigue rather than shape memory fatigue, is given as follows in which NiTi alloys are often used as an example.

Similar to other materials, the fatigue properties of SMAs are affected by many factors, such as the deformation strain and frequency, specimen geometry, microstructure, applied stress, temperature, working environment, and etc [236-244]. For example, the rotating-bending fatigue life of a NiTi SMA is shorter in air than that in water, and decreases with increasing the strain amplitude [245]. The fatigue threshold ΔK_{th} decrease linearly with increasing the stress ratio $R = K_{min}/K_{max}$, while the slope is affected by the temperature [240]. The dependence of low-cycle fatigue life on the temperature is stronger than that on the environment, such as corrosion fatigue in water does not appear [244]. Thermally cycled Ni-Ti SMAs within the R-phase transformation temperatures has a rather longer fatigue life than that in the other temperature range [246]. Effect of Ti_3Ni_4 precipitates on the fracture of NiTi SMA was studied in [247]: voids nucleate, grow and coalesce from

the Ti_3Ni_4 precipitates and the relative size of Ti_3Ni_4 precipitates is important. By repeating the combination of thermal and loading–unloading cycles on a $\text{Ti}_{50}\text{Ni}_{41.7}\text{Cu}_{8.5}$ alloy, it was found that the fatigue life is related to the dispersion strain energy (or dissipated work) E_d , the amount of decrease of recovery strain energy [248], while E_d decreases in inverse proportion to the increase in the twinning stress with decreasing the temperature [244]. However, it is much clear that much additional work is expected to achieve a complete understanding of the fatigue behaviors of SMA.

To predict the fatigue life, the most valuable information is the variation in da/dN , the crack growth rate per cycle, with the nominal stress-intensity range ($\Delta K = K_{max} - K_{min}$). It generally obeys the Paris power-law-like formulation $da/dN = C (\Delta K)^m$, where C and m are the material scaling constants and can be measured with fatigue experiments [249]. From the application point of view, the fatigue threshold ΔK_{th} , representing the nominal stress intensity range below which fatigue cracks are presumed not to propagate, is more important. Experimental results [243] showed that at 37 °C, the fatigue threshold ΔK_{th} of a typical $\text{Ni}_{50}\text{Ti}_{50}$ SMA ($R = 0.1$, 10Hz in air) was $2 \text{ MPa}\sqrt{m}$, and when the nominal SIF was increased to $\sim 30 \text{ MPa}\sqrt{m}$, the fatigue became unstable prior to failure. Between them, the crack growth rate satisfied the Paris power-law-like formulation while the Paris exponent ‘ m ’ was about 3.

Quite a few investigations have been focused on the effect of phase transformations on the fatigue properties in SMAs but different results were presented. A full field finite element (FEA) analysis [250] under the small scale transformation condition (the phase transformation zone is much smaller than the crack length) indicated that the fracture

toughness was enhanced by the martensitic transformation, particularly when the transformation is irreversible. It was claimed that the phase transformation reversibility could significantly reduce the increase in the fracture toughness. This so-called fracture toughening mechanism by the martensite transformation in SMAs was supported by theoretical analyses [251, 252], in which the constitutive model [253] was applied under different far field loading conditions to SMAs. By assuming the transformation volume strain effect on the crack tip SIF is negligible, the martensitic transformation-induced stress field reduces the crack tip SIF so as to improve the fracture toughness. Nevertheless, soon later, different conclusion was given in [254] that if taking into account the volume contraction during the martensite transformation, though less than 0.5% in NiTi SMAs [240, 255, 256], a considerable increase in the crack tip SIF is produced thus decreases the fracture resistance. The latter theoretical calculation was coincided with earlier experimental results [239, 240, 245, 257] that lower fatigue threshold, shorter fatigue life and faster crack growth rate were obtained in the stress-induced martensitic regions in SMAs. It was also confirmed that if the volume change during the SIM transformation was positive, such as in the Fe-Ni-Al SMA [258], the fracture toughness was reduced.

The effect of transformation temperature on the fracture toughness was complex. It was found that ΔK_{th} increased with increasing the temperature [240] in the condition of temperatures lower than M_d , which is the highest temperature for SIM transformation to take place. There was no significant change in ΔK_{th} in the temperature range from M_s to M_f , implying that the low fatigue threshold was due to the SIM transformation. On the other side, the fatigue threshold ΔK_{th} of Ni₅₀Ti₅₀ alloy increased with lowering the temperature from $\sim 2 \text{ MPa}\sqrt{\text{m}}$ at 37 °C to $3 \text{ MPa}\sqrt{\text{m}}$ at -65 °C, and to $\sim 5 \text{ MPa}\sqrt{\text{m}}$ at -196 °C,

respectively [239]. Melton and Mercier [259] claimed there was no significant dependence of fatigue life on the transformation temperatures, but in [257] it showed that both the crack growth rate and fatigue threshold were strongly related to the transformation temperatures. Finally, it was suggested in [237] that in SMAs, the effect of SIM transformation should be considered in order to understand the fatigue mechanism. Three temperature ranges should be distinguished when the effect of temperature on the fracture toughness is discussed, which are $T < M_f$ (stable martensite), $M_s < T < M_d$, and $T > M_d$ (stable austenite), respectively. Comparatively, the stress induced martensite has the lowest fatigue thresholds and shortest fatigue life.

From microstructural point of view, the fatigue resistance of SMA is related to the difficulty of defects generation and/or accumulation during thermally active or stress induced martensitic transformation cycles [238]. In the twinning structures, the high stress concentrations provided by the twinning structures have long been recognized as potentially important in crack nucleation. Sometimes, microcracks form at places where a twin reaches a free surface, and it may be the root cause of the mechanical failure [247]. Cracks prefer to nucleate at the martensite variant boundaries [260] or twin-twin intersections [210] under fatigue loading, as shown in Fig. 2.16. Müllner et al. [261] proposed a model that the highest stress exists when the growth of a twin is prevented, e.g. by a barrier twin, results in twin dislocations pile-up, produces a very high, static stress field, and causes crack initiation. For the thermally induced martensites, the phase boundaries between martensite and austenite provide additional source of localized internal stress concentrations [259]. Hornbogen [237] found that though the SMA appears highly damaged by these microcracks, it took a very high number of cycles before a macroscopic crack developed.

Figure 2.16. Initiation of cracks by repeated phase transformation [238] (a) multiple cracks nucleation at twin domain boundaries (as the arrows indicate) in a CuZnAl martensite, (b) schematic of nucleation sites of the fatigue cracks in martensite.

Chapter 3 Material properties characterization

The physical properties of the Ni-Mn-Ga FSMA, including the crystal structure, strain, transformation temperatures, magnetization, and mechanical properties were characterized by using appropriate techniques such as XRD, DSC, TMA, VSM and mechanical testing machine. The main purpose was to ensure that the Ni-Mn-Ga single crystals under study satisfy the criteria of the MSM effect. The experimental procedures and results are presented in this Chapter.

3.1. Composition and crystal structure

All the single crystal Ni-Mn-Ga specimens used in this research were provided by the AdaptaMat. Ltd., Finland, prepared by a modified Bridgman method. The faces of the as-received bulk prismatic were nearly parallel to the [100], [010], and [001] directions of the austenitic $L2_1$ unit cell ($Fm3m$ space group), respectively. Some specimens were further cut into smaller square pieces along the $(001)_c$ plane by the electro-discharge machining (EDM) method. The chemical compositions were analyzed on a Leica S360 SEM equipped with energy dispersive X-ray (EDX). The results, along with the transformation temperatures and Curie temperature of the specimens, are listed in Table 3.1. There was a slight departure from nominal composition along the $[001]_c$ direction (the growth direction), which was likely due to the Mn evaporation during fabrication [262, 263].

Table 3.1: Chemical composition, transformation temperatures, Curie temperature T_c and valence electron to atom ratio of the studied alloys

Sample	Chemical composition	A_s (°C)	A_f (°C)	M_s (°C)	M_f (°C)	T_c (°C)	e/a
S-1	Ni _{50.6} Mn _{30.7} Ga _{18.7}	35	41	33	29	74	7.78
S-2	Ni _{49.5} Mn _{28.9} Ga _{21.6}	48.9	49.6	43.4	42.6	96	7.62
S-3	Ni ₅₁ Mn _{30.4} Ga _{18.6}	38.5	47.0	32.5	23.5	83	7.80
S-4	Ni _{50.6} Mn _{28.2} Ga _{21.2}	39.8	48.2	38.6	33.7	85	7.71
S-5	Ni _{50.3} Mn _{28.7} Ga _{21.0}	47	51	43	39	100	7.67

The crystal structure of the low temperature phase was studied by X-ray diffraction at room temperature with a Philips diffractometer (PW1830, CuK $_{\alpha}$ radiation). The diffraction patterns were recorded from 20 to 80° at a rate of 0.02° per second. In a typical XRD pattern as indexed in Fig. 3.1, the main peaks correspond to a tetragonal unit cell with lattice constants $a = b = 0.594$ nm and $c = 0.557$ nm thus the tetragonality is $c/a = 0.938$. Assuming there is a $5M$ superlattice structure, the orthorhombic unit cell are refined as $\mathbf{a}_o // [1-10]_c$, $\mathbf{b}_o // [110]_c$ and $\mathbf{c}_o // [011]_c$ and lattice parameters $\mathbf{a}_o = 1/\sqrt{2} \mathbf{a}_c = 0.42$ nm, $\mathbf{b}_o = 5/\sqrt{2} \mathbf{a}_c = 2.1$ nm, and $\mathbf{c}_o = \mathbf{c}_c = 0.557$ nm. The subscript ‘ o ’ denotes the orthorhombic unit cell and ‘ c ’ the cubic unit cell. Some other aspects of the martensitic transformation in Ni-Mn-Ga FSMA are discussed in Appendix A.

Figure 3.1. The X-Ray diffraction pattern of $\text{Ni}_{50.6}\text{Mn}_{30.7}\text{Ga}_{18.7}$ at room temperature

3.2. Thermal properties

3.2.1. Transformation temperatures

Phase transformation temperatures of the Ni-Mn-Ga specimens were measured using a differential scanning calorimeter (TA Instruments, MDSC 2920). Before the experiments, temperature and heat flow were calibrated with indium as a standard reference. The samples were grinded (to have a mass in the range of 10~50 mg and to get a relatively flat plane), cleaned in acetone and dried. The sample was placed in an aluminum capsule and then put in the chamber while another empty one was used as the reference. It was initially heated rapidly to 150 °C, much higher than the A_f temperature, for 2~5 minutes to ensure it absolutely austenitic, and then the thermal cycles were ran between -60 °C and 150 °C. By observing the difference in heat flow between the sample and reference, DSC measures the amount of heat flow absorbed or released during the phase transformations. During the

measurement, N_2 and A_r gases were allowed to flow through the chamber to control the heating and cooling rates, or the temperature rate.

DSC results shown in Fig. 3.2 reveal a reversible phase transformation in sample S-1 accompanied by the well-defined thermal peaks. Transformation temperatures were determined to be $A_s = 35^\circ\text{C}$, $A_f = 41^\circ\text{C}$, $M_s = 33^\circ\text{C}$, and $M_f = 29^\circ\text{C}$, respectively, by the slope line extension method on the transformation peaks. The temperature hysteresis ($\Delta H = A_s - M_f$) between the forward and reversal transformations was $\sim 6^\circ\text{C}$ when the temperature rate was set at $2^\circ\text{C}/\text{min}$ in this experiment. The results for the other specimens are listed in the table 3.1. The M_s temperatures and chemical compositions (or valence electron) satisfy the empirical linear function, which is given in section 2.3.1.

Figure 3.2. The transformation temperatures of $Ni_{50.6}Mn_{30.7}Ga_{18.7}$ were determined to be $A_s = 35.01^\circ\text{C}$, $A_f = 41.14^\circ\text{C}$, $M_s = 33.41^\circ\text{C}$, and $M_f = 29.08^\circ\text{C}$ according to the DSC results [264].

3.2.2. Transformation strain

A thermomechanical analyzer (TA Instruments, TMA2940) was employed to obtain the strain–temperature relation during the phase transformation. A scheme of the crystal structure transition during the martensitic transformation is shown in Fig. A1. The dimensional change (Δl) along the measured direction was recorded with changing the temperature. The strain was defined as $\varepsilon = \Delta l / l_0$ where l_0 is the original length. A compressive stress of ~ 0.03 MPa was applied throughout the tests to hold the samples, and its effect on the deformation strain was ignored. The temperature rate was set at $5^\circ\text{C}/\text{min}$. As shown in Fig. 3.3, a elongate strain of around 2% was detected along the $[001]_c$ direction upon cooling and the strain was fully recoverable in the reverse transformation.

Figure 3.3. A recoverable strain of 2% was obtained along the $[001]_c$ direction during the forward and reverse phase transformations [48].

3.3. Surface morphology

Martensitic morphologies were observed by light ZEISS model optical microscopy or scanning electron microscopy (SEM, JEOL JSM-5600LV) at room temperature. Figure 3.4a shows the optical micrograph of sample S-1 in which twin bands display parallel with the band width of 10-50 μm . The relief was a reflection of the twin-related microstructure, showing the alignment of the twin variants. After thermal cycling over the transformation temperature range, different twin systems are found coexisting in the specimen. In most cases, the twin bands are self-assembled, as shown in Fig. 3.4b, crossing to each other and accommodate well. In some cases, however, cracks are found.

Figure 3.4. Martensitic morphologies of Ni-Mn-Ga single crystals under optical and SEM microscopes: (a) parallel displayed twin variants, (b) coexistence of differently oriented twin variants [264], and in (c) and (d) the SEM images of the specimen after etching showed similarity in the surface morphology.

Before SEM observations, the sample was carefully polished by using a series of diamond pastes to obtain an average roughness less than 0.1 micron (final polish sand paper), followed by etching in the solution (2% nitric acid + 98% methanol) for 20 minutes. The true morphologies after cleaning and drying (SEM images Fig. 3.4c and 3.4d, observed on the same surface) showed some similarities. The twin variants aligned in the single twin system, or self-accommodated in multi twin systems. Obviously, to achieve larger shape memory strain, the martensitic structure shown in Fig. 3.4c is expected.

3.4. Magnetic properties

3.4.1. Magnetic susceptibility

A magnetic susceptibility meter (Bartington Instruments, MS2 system) was used to characterize the temperature dependence of the low-field magnetic susceptibility (χ). The heating and cooling rates were controlled to be as low as less than 1 °C/min. The experimental results of sample S-2 are shown in Fig. 3.5.

The magnetic susceptibility exhibits rather sharp changes as expected not only on the ferromagnetic-paramagnetic transition, but also during the phase transformation. The reason of latter arose from the change in magnetic anisotropy associated with the structural phase transition [73, 77, 176]. According to the magnetic susceptibility curve, the Curie temperature of sample S-2 was estimated to be 96 °C, and the phase transformation temperatures were $A_s = 42.7$ °C, $A_f = 45.1$ °C, $M_s = 41.1$ °C, and $M_f = 39.2$ °C, respectively. The phase transformation temperatures coincided well with the DSC results (not

presented). Above the Curie temperature, the magnetic susceptibility dropped to almost zero, indicating the entire degeneration of spontaneous magnetization. The measurement results of T_c of the other samples are also listed in Table 3.1.

Figure 3.5. The magnetic susceptibility χ of $\text{Ni}_{49.5}\text{Mn}_{28.9}\text{Ga}_{21.6}$ as a function of temperature. The Curie temperature and phase transformation temperatures were characterized by the drastic changes in the magnetic susceptibility [48].

3.4.2. Field dependence of magnetization

Magnetization curves as a function of magnetic field were measured by using a vibrating sample magnetometer (VSM, Lakeshore 7300 system) with the maximum field strength of 13 kOe and sensitivity of 10^{-3} emu. VSM measures the magnetization change generated by the moving sample in an electromagnetic field. The experiments were carried at room temperature on sample S-1 and S-2 and large magnetocrystalline anisotropy was confirmed. More importantly, the results indicated that the magnetization properties were strongly related to the microstructure. However, since the samples were not compressed to a single variant configuration before the measurement, the magnetic anisotropy constants could not be calculated from the M–H curves [38, 90].

Magnetizations of sample S-1 along both $[001]_c$ (easy axis) and $[100]_c$ (hard axis) directions were measured under the magnetic field varying from -12 kOe to $+12$ kOe. Only the first quadrant with increasing the magnetic field from zero to 12 kOe (Fig. 3.6a) was presented since the curve was symmetrical to the origin of coordinates. Magnetization saturation was not achieved in both directions due to the limitation of the applied field strength. By normalizing to the sample weight, the highest magnetization in easy axis and hard axis was calculated to be ~ 34.15 emu/g and ~ 70.47 emu/g, respectively, at the maximum magnetic field strength achievable, exhibiting giant magnetocrystalline anisotropy. Furthermore, there was a more complex ‘step-like’ increase of magnetization in the $[001]_c$ direction within the range O-A-B and B-C-D as labeled in the curve.

Two independent processes, magnetic domain wall movement (in weak field) and magnetization rotation (in strong field), are the major magnetization mechanisms in most ferromagnets [265]. But for FSMA, if the MAE in a strong field is large enough compared to the energy required for the twin boundary motion, magnetization rotation can be bypassed while the magnetization remains in the original easy axis of the reoriented variant, along with the applied magnetic field. In the VSM experiment, the strength of the applied magnetic field increased continually from zero to the maximum. Therefore, the recorded increase in magnetization should be related to not only the movement of the magnetic domain walls but also the twin boundaries movement. Assuming that the magnetization rotation and twin boundary motion were controlled separately by the external magnetic field, the above ‘step-like’ magnetization can be explained by considering the coexistence of several twin systems of differently oriented (see Fig. 3.4). The critical magnetic energy (field strength) needed to initiate the twin boundary motion

depends not only on the angles between easy axes of the twinned-related variants, but also on the angle between variant and external magnetic field [114]. Therefore, the switch fields are different among the differently orientated twin systems coexisting in the specimen due to the previous thermal cycling. Before the magnetic field was strong enough to induce the twin boundary motion the magnetization (M) increased by magnetic moment rotation in each twin system. However, accumulation of MAE difference ΔK_u with increasing the field strength (H) increased and finally induced the twin boundary motion. The magnetic-energy-favorable twin variants grew at the expense of other twin variants. Consequently, it provided new space for the increase in magnetization because the structural deformation will doubtlessly affect the magnetic domains walls, resulting in the distinct change in magnetization. Magnetization saturation for this twin system was achieved under this field strength but it was only a metastable state for the whole system. The crystallographic deformation in other twin systems will further influence it unless the specimen consisted of only one variant. In a word, the magnetization increase in conventional ferromagnets is continuous and smooth, while that by the twin boundary motion was discontinuous and sharp. One can conclude that the coexistence of differently oriented twin systems is responsible for the abnormal ‘step-like’ magnetization. And since MFIS is almost linear with magnetization before saturation, some similar ‘step-like’ strain vs. magnetic field curves reported in [123, 266] may provide positive support to this view.

The magnetization curve of sample S-2 (Fig. 3.6b) shows that the saturation field along the $[100]_c$ and $[001]_c$ directions is quite different. Large transient hysteresis occurred in the first quadrant, which was a typical and unequivocal sign of the MSM effect. The saturating field was 2 kOe for $[001]_c$ easy axis and 8 kOe for $[100]_c$ hard axis, the highest magnetization was ~ 71 emu/g after normalizing the weight, and the switch field was ~ 6.4

kOe, as indicated by the arrow. The effect of magnetic field on the martensite reorientation, or namely the magneto-microstructural mechanism, has been illustrated in [118]. Such a process causes the rapid growth of the magnetically preferred twin variants so that the magnetization increases steeply. It is worth noting that the jump in the magnetization curve showed once only when increasing the field strength from zero to the maximum value. Decreasing it to zero and reloading the magnetic field would not repeat the magnetization jump if the relative position and angle of the specimen to the magnetic field was not changed.

Figure 3.6. Magnetization as a function of the magnetic field in (a) $\text{Ni}_{50.6}\text{Mn}_{30.7}\text{Ga}_{18.7}$: the ‘step-like’ increase implies a multi twin system structure [264] and in (b) $\text{Ni}_{49.5}\text{Mn}_{28.9}\text{Ga}_{21.6}$: twin boundary motion was evidenced by a drastic increase in magnetization at the field of 6.4 kOe [48].

3.4.3. Temperature dependence of magnetization

The temperature dependence of magnetization was simply undertaken under a constant 0.5 T magnetic field because there was no temperature control unit in the VSM system. The sample was heated to 120 °C and cooled by air. During cooling, the magnetization was detected by a Hall probe aligned closely to the sample surface. The results are shown in Fig. 3.7. The Curie temperature was determined to be about 110 °C according to the curve. With lowering the temperature, the magnetization increased almost linearly and a large jump followed, characterizing the transformation temperature $T_m \approx 40$ °C. The curve also indicated that $T_m < T_{ca} < T_{cm}$ in this specimen according to [176], while T_{ca} and T_{cm} are the Curie temperature in the austenitic phase and martensitic phase, respectively.

Figure 3.7. Temperature dependence of magnetization of $\text{Ni}_{50.6}\text{Mn}_{30.7}\text{Ga}_{18.7}$ under a constant magnetic field of ~ 0.5 T.

3.5. Magnetomechanical properties

The stress-strain curves were characterized with and without the application of magnetic field to investigate the effect of magnetic field on the shape memory strain. The sample S-5 was deformed under uniaxial compression and unloaded at a strain rate less than $5 \times 10^{-5} \text{ s}^{-1}$ in a mechanical testing machine (Instron) equipped with a 50 N load cell at room temperature. As illustrated in Fig. 3.8, the sample was mounted onto a nonmagnetic holder with the longest edge parallel to the compression axis (z-direction), and the magnetic field was applied in the x-direction, parallel to the shortest edge of the sample. The strain was measured along the z-direction. The magnetic field $H \sim 0.5 \text{ T}$ was produced by an in-house built permanent magnet system from eight disc-shape Nd-Fe-B magnets with diameters of 100mm. A Hall probe was located close to the sample perpendicular to the x-direction. The resolutions were better than 0.1 N, 0.1 micron, and 0.1 mT in force, displacement, and magnetization, respectively. Before testing, the sample was heated to 80 °C and then cooled to room temperature under a magnetic field of 0.3 T.

Figure 3.8. Schematic diagram of the compressive loading and unloading test.

The compressive deformation results were plotted in Fig. 3.9. With or without applying the magnetic field, there were typical plateaus in the stress-strain curves indicating the detwinning process. However, the detwinning stress increased from ~ 1 to ~ 2.5 MPa ($\Delta\sigma_{\text{mag}} \sim 1.5$ MPa) when the magnetic field was applied since the twin variants reorientation driven by the mechanical stress was retarded by the magnetic force. Only a few fraction of the deformation strain was recovered upon unloading in the mechanical only compression. The detwinning strain was permanent since there was no restoring stress. Comparatively, almost full recovery occurred under the magnetic field. Obviously, it was the magnetic force driving the material back to its origin microstructure. The 0.5 T magnetic field may be not strong enough to finish the procedure so that there were still some irreversible strains ($< 0.5\%$) left. The deformation did not produce a maximum strain of 6%, implying the specimen was not in the single variant configuration. There was a difference in the maximum strain between two cases because the strain was not fully recovered after the mechanical only deformation thus the original length was different.

Figure 3.9. Stress-strain curves of the $\text{Ni}_{50.3}\text{Mn}_{28.7}\text{Ga}_{21.0}$ single crystal under compressive deformation with and without the application of an external magnetic field of 0.5 T. [267]

3.6. Summary

In this chapter, the structural, thermal, magnetic and mechanical properties of Ni-Mn-Ga alloys were investigated. The results proved that the studied Ni-Mn-Ga alloys exhibited (1) phase transformation with the transformation temperatures slightly above the room temperature and a reversible transformation strains up to 2% (2) magnetic transition at the Curie temperature; (3) large magnetocrystalline anisotropy; (4) low detwinning stress of ~ 1 MPa and its increase under the external magnetic field. In short, these alloys were typical FSMA.

Chapter 4 Thermomechanical stability of Ni-Mn-Ga single crystals

The significance of Ni-Mn-Ga FSMA is that their martensite twin boundary can be driven by a modest magnetic field [7, 45, 268]. A reversible MFIS is achievable through rotation of magnetic field that drives the martensite twin boundaries back and forth via switching the crystal lattice. Ni-Mn-Ga FSMA also exhibit the two way memory effect (TWME) during thermal cycling [51, 67, 127, 137], some with a ‘step-like’ behavior in the temperature-strain curves. Generally, the origin of TWME is related to the orderly distributed dislocation arrays generated during a ‘training’ process. The resulting internal stress field plays a key role in the occurrence of TWME through promoting the formation of preferentially oriented martensite variants in the stress direction [269-271].

It was recently reported that during some stress-free thermal cycles, the shape memory strain of Ni-Mn-Ga FSMA suddenly changed from elongation to contraction or vice versa. This was explained as a result of the change in the internal stress field [51, 52]. Such abnormal phenomenon has seldom been observed in other type of SMA. It has also been reported that MFIS gradually increased after several hundreds cycles of rotating magnetic field [272] and it can be affected by the rate of increasing field strength [118]. Cyclic deformation can introduce internal stress field and consequently redistribute the martensite variants. The mechanism seems to be similar to the martensite reorientation in NiTi SMA through mechanical cycling [273].

However, the mechanism of how the internal stress field affect shape memory strain has not been clearly explained. In this chapter, the TWME of Ni-Mn-Ga single crystal under different thermomechanical conditions was investigated. The factors affecting the internal stress field and the stability of TWME were studied. The mechanism of strain instability was proposed by taking into account the internal stress-induced redistribution of martensite variants.

4.1. Stability of TWME during thermal cycling

The specimens used in this research were cut from sample S-2 ($\text{Ni}_{49.5}\text{Mn}_{28.9}\text{Ga}_{21.6}$). Thermomechanical analyses were carried out between 10 °C to 70 °C to cover the transformation region, mainly at two different temperature rates (heating and cooling rates), namely 2 °C/min and 5 °C/min. Sample surface was polished and etched before tests in order to observe the martensite variant distribution. A compressive stress of ~0.03 MPa was applied throughout these tests to hold the samples, and its effect on the deformation strain was ignored. The specimen exhibited a stable TWME when the temperature rate was 2 °C/min with a contractive strain of 2% almost fully recoverable during the 15 thermal cycles (Fig. 4.1a). This transformation strain was repeatable for over 200 cycles. The surface morphology under optical microscopic observation did not show any change before and after thermal cycling. Nevertheless, when the temperature rate was increased to 5 °C/min, the shape recovery became inconsistent (Fig. 4.1b). The transformation strain varied in the range from -4% to 2% during thermal cycling. In the first six cycles, the strain versus temperature curves (Fig. 4.1c) were almost unchanged despite slight variation in the maximum strain (about -2%). The strain jumped to about -4% (Fig. 4.1d) in the seventh cooling

process, almost double the magnitude of the previous cycles. After that, strains of -2% and -4% appeared in the subsequent cycles; the strain suddenly reversed from contraction to expansion during the 13th cooling process, similar to the results reported in [51, 52]. In the subsequent thermal cycles the strain response became very irregular. More details of strain variation as a function of thermal cycling are shown in Fig. 4.2a. Since the mechanically applied stress during TMA test was negligibly small (~ 0.03 MPa), the irregularity occurring to the TWME at $5^\circ\text{C}/\text{min}$ could only be attributed to the increase in the temperature rate. Besides, the strain irregularities of the latter sample remained even after the temperature rate was reduced back to $2^\circ\text{C}/\text{min}$.

Figure 4.1. TMA results under two temperature rates: (a) 15 thermal cycles at 2 °C/min and (b) 20 thermal cycles at 5 °C/min. Several typical strain-temperature curves in (b) are highlighted in (c) and (d) [274].

The effect of thermal cycling on M_s is plotted in Fig. 4.2b and the change in M_s is generally attributed to the internal stress accumulation. The M_s temperatures were determined by the slop-line-extension method from TMA curves. When the temperature rate was 2 °C/min, M_s was higher than that under 5 °C/min, and it increased slightly with thermal cycling. The maximum increment was less than 0.3 °C in 15 cycles. Comparatively, M_s increased more sharply under 5 °C/min, about 0.7 °C in 5 cycles (cycle 3~7). Then, M_s decreased in the next two cycles. However, a similar process (cycle 9~13) was repeated in which M_s increased again to a maximum value in 5 cycles. It was interesting to note that each M_s maxima/minima corresponded to an irregular strain jump, as shown in Fig. 4.2. For example, the maximum M_s (35.1 °C) accompanied by a strain jump to -4% in the 7th cycle. The effect of thermal cycling on the martensitic transformation temperature involves several mechanisms with opposite effects [55] and will be discussed in the next section.

It was found that applying external load can stabilize the TWME. The temperature rate was set to 5 °C/min on a specimen with initially irregular recovery strains at this rate. Compressive stresses from zero to ~0.5 MPa were applied step by step, and each step consisted of five thermal cycles. Strains as a function of temperature under different stresses are shown in Fig. 4.3. The stability of TWME was improved progressively with increasing the stress. Finally, when the applied stress reached 0.5 MPa, the strain-temperature curve was stable. Cherechukin et al. [121] reported that the recovery strain of a $\text{Ni}_{2.16}\text{Mn}_{0.80}\text{Fe}_{0.04}\text{Ga}$ specimen increased with thermal cycling. The specimen used was polycrystalline and a stress of about 3 MPa was applied. The TWME strain was small (~1.75%) in the first cycle. It is thus understandable that the

TWME increased with thermal cycling and saturated at the maximum value due to the stress-induced preferentially oriented martensite variants.

Figure 4.2. (a) Shape recovery strain (shown in Fig. 4.1b) as a function of thermal cycle. With thermal cycling, the strain becomes unstable and shows some irregularities. (b) M_s temperature as a function of thermal cycling under two temperature rates. M_s is determined using slop-line-extension method based on TMA curves in Fig. 4.1 [274].

Figure 4.3. Stress effect on the recoverability of strain versus temperature curve. With increasing the compressive stress from zero up to ~ 0.5 MPa, the curves became stable under thermal cycling. [274]

The Stability of TWME due to applied compressive stresses was further studied under different temperature rates. TMA tests under a constant stress of 0.25 MPa and several temperature rates between 0.5 $^{\circ}\text{C}/\text{min}$ and 15 $^{\circ}\text{C}/\text{min}$ were carried out and the results are shown in Fig. 4.4. When the temperature rate was low, the recovery strain presented good repeatability. However, an irregular elongation strain of $\sim 2\%$ (instead of a 4% contractive strain as in the previous cycles) appeared during cooling when the temperature rate was 12 $^{\circ}\text{C}/\text{min}$. The shape was recovered during the reverse transformation in the next thermal cycle (15 $^{\circ}\text{C}/\text{min}$). The experiment results coincide with the maximum theoretical strain of 6.25% for martensite reorientation [118]. Besides, it was noticed that the transformation temperatures shifted with increasing temperature rate.

Figure 4.4. TMA results show the effect of compressive stress (0.25 MPa) on the shape recovery for different temperature rates. [274]

The effect of temperature rate on the transformation temperatures and transformation enthalpy was also investigated by using DSC (Fig. 4.5a). The same temperature rates were chosen namely, 0.5, 1, 2, 4, 6, 8, 10, 12, and 15 °C/min. The results show that the temperature rate affects M_s and A_s temperatures slightly; whereas it has a strong influence on the M_f and A_f temperatures (Fig. 4.5b). The transformation enthalpy ΔH remained almost constant (~ 5 J/g) for all the heating rates. The shift in M_f and A_f temperatures is probably due to the thermal conduction process that leads to a temperature gradient in the specimen.

Figure 4.5. (a) DSC results under different temperature rates: 0.5, 1, 2, 4, 6, 8, 10, 12 and 15 °C/min, respectively. (b) Phase transformation temperatures and transformation enthalpy as a function of temperature rate. [274]

4.2. Discussion

Thermal cycling rearranges dislocations and increases dislocation density [275] such that the TWME may decrease gradually [271, 276]. The dislocations generated during

thermal cycling eventually reduce the reversibility of the thermoelastic phase transformation. However, degradation of TWME under thermal cycling is rather different from the irregular TWME observed in this work which has never been reported in conventional SMAs. In this work, the internal stress field developed during thermal cycling is analyzed and its effect on the martensite variants reorientation is considered.

The effect of stress on the martensitic transformation can be calculated through the modified Clausius-Clapeyron equation [55],

$$\frac{d\sigma}{dT} = -\frac{\Delta S}{\Delta \varepsilon} = -\rho \frac{\Delta H}{\Delta \varepsilon \cdot T_0} \quad (4.1)$$

where σ is the uniaxial stress, $\Delta \varepsilon$ the transformation strain, ΔS the transformation entropy, ΔH the transformation enthalpy, and T_0 is the equilibrium temperature. By inputting the parameters $\rho = 7.22 \text{ g/cm}^3$, $\Delta \varepsilon \sim -4.1\%$, $\Delta H \sim 5.0 \text{ J/g}$ and $T_0 = 46.8 \text{ }^\circ\text{C}$, $d\sigma/dT$ is calculated to be about 2.7 MPa/K . It must be pointed out that the influence of temperature rate on $d\sigma/dT$ is ignored since T_0 and ΔH (Fig. 4) vary negligibly with the temperature rate in the first a few cycles. $d\sigma/dT$ is the temperature dependence of the critical stress needed to initiate the martensitic transformation, and its value is close to the stress dependence of M_s temperatures during thermal cycling [277]. Therefore, $\Delta \sigma_{int}/\Delta M_s = d\sigma/dT = 2.7 \text{ MPa/K}$ is used to estimate the accumulated internal stress (σ_{int}) with thermal cycling. M_s increased less than $0.3 \text{ }^\circ\text{C}$ after 15 cycles at $2 \text{ }^\circ\text{C/min}$, thus the accumulated internal stress was less than $0.3 \times 2.7 \approx 0.8 \text{ MPa}$. Comparatively, at $5 \text{ }^\circ\text{C/min}$, M_s increased relatively faster, for example, $0.51 \text{ }^\circ\text{C}$ in 5 cycles (3rd–7th) and the corresponding accumulated internal stress was about 1.4 MPa . It is

comparable to the critical detwinning stress (1~3 MPa). The reason why the effect of temperature rate on the internal stress has never been reported may be that the accumulated internal stress is too small to influence the shape memory effect of conventional SMAs.

The effect of stress on the martensite microstructure leads to two related processes: (a) the growth of martensite variant at the expense of unfavorable ones, and (b) the conversion from multi-domain to single-domain structure [109, 114]. There are three possible twin variants (V1, V2 and V3) in the Ni-Mn-Ga martensitic tetragonal lattice, with the c axes parallel to the $[001]_A$, $[010]_A$ and $[100]_A$ directions of the parent phase, respectively, as illustrated in Fig. 4.6. Assuming that the measuring direction is along $[001]_A$, the strain in this direction is thus determined mainly by the volume fraction of V1. This strain can be affected by the transition between (twin-related) V1 and V2 within the V1-V2 twin domain, as well as the conversion between V1-V2 to V2-V3 twin domains. The latter has been suggested in [109, 272]. The variant redistribution can be induced by the accumulated internal stress in thermal cycling. When the variant redistribution occurs during martensitic transformation the irregularity in recovery strain appears. Accordingly, once the variant redistribution occurs the accumulated internal stress is relaxed, implied by the decrease in M_s in the next cycle, and the irregularity disappeared. The stresses needed to reorient the martensite variant in single domain and multi-domain structures are different [109, 118].

In light of above considerations, the TMA results can be explained as follows. When a specimen in the austenitic state (Fig. 4.6a) is cooled, martensite plates nucleate from

the parent phase. Under the stress free condition, differently orientated martensite variants are formed as indicated in Fig. 4.6b in a self-accommodation way to minimize the elastic energy. In this case, differently oriented twinned variants have almost the same volume fractions (Fig. 4.6e), and consequently the shape change is about 2% contraction along the $[001]_A$ direction. During the reverse transformation, path 1 is followed. The internal stress accumulated during thermal cycling may promote the growth of variant 1 which has the shortest length along the $[001]_A$ direction (Fig. 4.6c). If the internal stress is high enough, the specimen becomes a (quasi-) single variant (Fig. 4.6f), with a maximum contractive strain and the path 2 is followed. The other possibility is a transition between a single domain (V1-V2) and multi-domain (V1-V2 and V2-V3) structures. If a twin domain consisting of V1-V2 is nucleated at the initial cooling process it will result in a contractive strain. Later, the transition from V1-V2 domain to V2-V3 domain (Fig. 4.6d) produces an elongation strain due to less V1. Finally, if the specimen consists of a single domain of V2-V3 (Fig. 4.6g), there is a valley in the TMA curve allowing the strain changes from contractive to extensive, as shown by path 3.

Preferential orientation of martensitic variants plays an important role in obtaining the large transformation strain during martensitic transformation. External stress promotes the preferential orientation of martensite variants and the TWME [47, 61, 114]. For example, under compressive stress along $[001]_A$ direction, V1 is more preferable than the other two variants because it gives larger contraction strain along the stress direction. Therefore, with increasing compressive stress during thermal cycling, the strain-temperature curve becomes more stable, as is confirmed by the experimental results in Fig. 4.3. However, high temperature rate and high

accumulated stress result in the redistribution of martensite variants and irregularity in the shape memory strain.

Figure 4.6. A schematic diagram of effect of martensite variant reorientation on the recovery strain. [274]

4.3. Summary

The effects of temperature rate, thermal cycling and external load on the TWME of the Ni-Mn-Ga single crystal have been studied.

- 1) Stability of the TWME is affected by the temperature rate and external stress.

High temperature rate results in irregularity in TWME. A proper external stress can help stabilize the TWME.

- 2) The transformation temperatures vary with thermal cycling, which implies an internal stress accumulation. The accumulated internal stress is evaluated with

$\Delta\sigma_{int}/\Delta M_s = d\sigma/dT = 2.7 \text{ MPa/K}$. At higher temperature rate, the accumulated

internal stress is comparable to the critical detwinning stress (1~3 MPa) of Ni-Mn-Ga FSMA.

- 3) The irregularities in TWME are due to the internal-stress-induced martensitic variants rearrangement. An explanation is proposed to relate the shape memory strain to the redistribution of martensite variants by taking into account the accumulated internal stresses.

Chapter 5 Fatigue behavior of Ni-Mn-Ga FSMA under Thermal Cycling

Cleavage fracture occurs occasionally when the Ni-Mn-Ga single crystals are cyclically deformed under the magnetic field and more often when the MFIS is large [40, 41]. When the MFIS is up to ~6%, the fatigue life is only a few thousands, which is much shorter than the expected. What's worse is that this material is prone to fracture under thermal cycling through the phase transformation temperature. The poor magneto-/thermo-mechanical fatigue property of Ni-Mn-Ga FSMA is a serious drawback for their engineering applications. In this chapter, failure procedures of Ni-Mn-Ga single crystals are described based on the microscopic observations on the fracture planes and surfaces. The effects of thermal cycling and twin related microstructure on the thermomechanical fatigue property are investigated and the fatigue mechanism is proposed.

5.1. Failures of the Ni-Mn-Ga single crystals

Upon fracture of sample S-1 as a result of cyclic deformation under a rotating magnetic field at room temperature, the fracture plane was observed to have a slope intersecting the front surface at an angle of about 45°. Using optical microscopy, the angles between the fracture plane and the front surface, which was parallel to the (100)_c plane, were measured to be 48.18° and 49.36° on the two sides, respectively (see Fig. 5.1, only one side is shown).

Figure 5.1. Schematic representation of twin boundary motion (Left) and optical microscopical image of the specimen (Right), θ is the angle between fracture plane and the front surface. The inset shows the specimen on a stage. [264]

During the MSM effect, there is always an energy balance between the magnetic energy input and mechanical work output. If the directions of the magnetic field and that of the stress field are perpendicular to each other, a mobile plane is formed which separates two parts favored by either field. This mobile twin boundary allows the material to switch between two states, as shown in Fig .5.1 (left). In either state, the twin boundary motion can sweep the entire specimen until reaching the surface or being pinned by defects. Therefore, in the condition that boundary moves between two pinning sites, the stress on the separating plane is purely a shear stress [202]. The shear angle is a function of the tetragonality of the martensite unit cell,

$$\theta = \frac{a^2 - (c/\sqrt{2})^2}{a(c/\sqrt{2})} \quad (5.1)$$

The value of θ was calculated to be 48.42° when $a = 0.594$ nm and $c = 0.557$ nm, which was rather close to the measured values. In Murray's model [202], this angle is also the one along which the twin plane interacts with the unit cell. This coincidence implied that

the crack propagation was along the mobile plane (a similar conclusion was given in [41]), and accordingly the shear stress plays a great role.

As for the specimen S-2, after each TMA run at the rate of 2 °C/min as described in the previous chapter, the surface morphology was observed with an optical microscope. Microscopic observation of the specimen in as-received condition (before further polishing) showed that the specimen consisted of twin bands of the same orientation. Some twin bands were interrupted by a pre-existing crack, as shown in Fig. 5.2a. This uniformity of the twin bands distribution was altered by the first thermal cycle (after polishing), and it was consequently noticed that the specimen consisted of two portions. One had twin bands of the original orientation, while the other consisted of twin bands with orientation almost normal to the original one, as seen in Fig. 5.2b. These two parts were separated by a macroscopic linear boundary throughout the specimen, which did not move significantly during the following thermal cycles.

Further SEM observation was focused on the tip of the pre-existing crack to see the effect of thermal cycling (Fig. 5.3a) on its crack propagation. The results showed that after two hundred thermal cycles, the crack propagated a short distance along its original direction, and some new cracks were also created in its front. The nearer crack was connected to the main crack via a branch, while another nearby crack grew separately to a considerable length. The interaction between the new crack and the branch produced a very narrow microcrack, as highlighted by a circle in Fig. 5.3a. Some zigzag crack propagation paths were found in other regions as shown in Fig. 5.3b, which were considered to be related to the twin structures [43]. New small cracks were also initiated at the junction points.

Figure 5.2. Optical micrographs of the Ni-Mn-Ga single crystal before the thermal cycle (a) and after the first thermal cycle (b). In (a), twin bands have the same orientation, while some were interrupted by a pre-existing crack of 0.68 mm. The angle θ is 42.7° . In (b), the specimen consisted of twin bands of two orientations nearly normal to each other. [48]

Figure 5.3. SEM micrographs. (a) Propagation of the pre-existing crack, introduction of the new cracks in front of the crack tip, and connection of the cracks. (b) Zigzag characteristics of the crack propagation path and new cracks initialization. [48]

However, under the temperature rate of $5^\circ\text{C}/\text{min}$ for less than 50 thermal cycles, remarkable changes were observed (Fig. 5.4a) in the martensite morphology in which differently oriented martensite twin bands formed. In one region, they were well accommodated with each other; but in another region of the same specimen, some cracks with length of $100\sim 150\ \mu\text{m}$ propagated along the similar direction, i.e. around 45° to the original twin bands (Fig. 5.4b). The cracks may have initiated from the specimen surface. In addition, a crack with width of $1\sim 2\ \mu\text{m}$ and length in the order of millimeter was

formed in the vicinity of main crack, as shown in Fig. 5.4c. Similar phenomena were observed in ferritic steels [278] and such narrow crack has been considered to have brittle cleavage character and referred to as ‘pre-cleavage microcrack’. The significant difference between the surface morphologies and crack behaviors after thermal cycling at two temperature rates indicated that such temperature rate plays an important role in the brittleness of Ni-Mn-Ga single crystal. The framed area in Fig. 5.4c is enlarged in Fig. 5.4d. It shows ‘jumps’ of the fracture plane into the adjacent parallel plane, which is one of the pre-cleavage microcrack features [278].

Figure 5.4. Under the temperature rate of 5 °C/min for less than 50 thermal cycles, (a) differently oriented martensite twin bands formed, as indicated by the arrows, and (b) in another region, some cracks with length of 100~150 μm were found. (c) A narrow microcrack was formed in the vicinity of main crack with brittle cleavage character. Enlargement (d) of the framed area in (c) shows ‘jumps’ of the fracture plane into the adjacent parallel plane. [279]

Sample S-3 fractured completely after several low-stresses (~ 1 MPa) bending deformations. Fig. 5.5 shows the SEM image of the fracture surface, which can be divided into three distinct regions with different morphology, as separated by the dash lines. In region I, benchmarks as a typical feature of fatigue were observed along the edge of the specimen. Fig. 5.6a shows that there were several striations in each benchmark, and generally, each striation presented the crack advancement in one loading cycle. The region II was relatively smoother but benchmark patterns were also observed at high magnification (Fig. 5.6b). However, the spreading direction of the striations was from left to right, or vice versa, different to that in region I (from bottom to upside). Besides, the crack growth rate ($1\sim 10$ $\mu\text{m}/\text{cycle}$) estimated from the striation pattern was much less than that in the Fig. 5.6a (> 20 $\mu\text{m}/\text{cycle}$). It was deduced that they were produced by different fatigue processes. According to the mechanical history of this sample, it was likely that the benchmarks in region I were attributed to the bending deformations, while those in region II were produced before the specimen was received. Finally, the material could not withstand the loads and fracture catastrophically with rough morphology (Fig. 5.6c and 5.6d). Comparing the SEM images in these two figures revealed that the directions of the twin bands were almost normal to each other, which confirmed the above surface observations. It proved that different twin systems coexisted in the same specimen.

Figure 5.5. Surface morphology of the fracture plane after several low stress (~ 1 MPa) bending deformations. Three regions were distinguished by the dash lines due to the drastic difference in the morphology.

Figure 5.6. SEM images of selected regions in Fig. 5.6: (a) typical surface morphology in region I, A is where crack initialized and B is the benchmark; (b) striation patterns in region II showed different direction to that in region I; twin bands exhibited in (c) and (d) after the catastrophic failure and they were normal to each other.

5.2. Discussion

5.2.1. Crack initiation

Lattice twins may nucleate microcracks [210]. Obviously, pile-up of large amount of twin dislocation makes crack initiation and propagation easier [210]. In terms of the crack initiation in the Ni-Mn-Ga martensite, a model has been proposed in which the cracks are initiated along the twin boundaries due to the movement and pile-up of a large amount of twin dislocations [41, 109], as illustrated in Fig. 5.7. Differently oriented twin variants are created from a single variant, acting as barriers to the dislocation motion in the major twin systems, and capture the twin dislocations if they are thick enough. Large local stresses are built up along the twin boundary with dislocations pile-up and cause the crack initiation on the habit plane of the barrier twin.

Figure 5.7. Schematic of the blocking of moving twinning dislocations along an incident twin boundary by a barrier twin [41]. With the growth of the incident twin structure, twin dislocations are accumulated on the barrier twin boundary and nucleate a crack.

The occurrence of twin-twin interactions [210] during thermal cycling can be another source of dislocations pile-up and microcrack initiation. In the previous chapter, the irregularity in TWME of Ni-Mn-Ga single crystal is evidenced with increasing the

temperature rate. It was suggested that the transition was attributed to redistribution of differently oriented twin variants. These twin variants may or may not accommodate well with each other. The sample surface was polished and then etched by 2% HNO_3 + 98% Ethanol solution after the TMA tests. The etching rate is faster at the place where the dislocation density is high, which are probably due to localized chemical attacking around the dislocation pile-ups. Thus twin boundaries display (Fig. 5.8a), exhibiting the twin variants well-accommodated. Nevertheless, some regularly distributed holes appeared, similar to the so-called ‘etch pit’, as shown in Fig. 5.8b. It indicated that the twin dislocations were mainly distributed on the twin variant boundaries and the reactions mostly occurred at the twin tip where differently oriented twin variants met. However, the intersecting twin systems may also introduce microcracks into the sample and occasionally results in cleaving pieces off of the sides of a crystal [38]. When the amount of dislocations was large enough, microcrack formed at the twin-twin intersections, as illustrated in Fig. 5.9c. Comparing Fig. 5.9b and 5.9d, in which cracks propagate along the intersection of different twins, the similarity between the locations of dislocation pile-up and the crack propagating can be observed. According to [210], the cracks formed at twin intersections have also been observed in Fe, Mo, and Cr single crystals and some alloys.

To further study the twin dislocation reaction when two twin boundaries meet, the topography of a region containing the ‘etch pit’ in Fig. 5.8b was studied by using atomic force microscope (AFM, Digital Instruments Dimension 3000). AFM observation was performed under contact mode. Fig. 5.9 shows a typical AFM image, illustrating deeper regions at twin-twin intersections and indicating the high dislocation density.

Figure 5.8. Differently oriented twin systems meet at the domain boundary and result in the twin-twin intersection. In (a), the twin systems accommodate well but in (b) stress concentration is produced at the junctions. (c) An illustration of the twin dislocation interaction resulting in dislocations to pile up at twin-twin intersection. (d) Crack propagation along the intersection of different twin systems.

Figure 5.9. Atomic force microscopic image of the etched surface indicates the high dislocation density at the twin-twin interaction.

Besides, thermal cycling on shape memory alloys may lead to the accumulation of dislocations on the austenite-martensite (A-M) interface and internal stress in the parent phase [280, 281]. These dislocations can be inherited by martensite. Localized sliding at the A-M interfaces and variants domain boundaries in martensite is often observed as a cause of crack formation [238].

5.2.2. Crack propagation

The crack propagation behavior of Ni-Mn-Ga FSMA should be strongly related to the martensitic microstructure. Since the direction of the shear stress is on the mobile twin plane, the crack may thus propagate along the twin plane. The twin plane can be any of the four $\{112\}$ planes in the martensite. However, under magnetic cycling, there are total six possible orientations because two unique twin planes are added since the c-axis can be rotated by roughly 90° in a transverse field. Crack can propagate along only one of these planes, depending on the orientations of the magnetic and stress field. Thus, the angle between the fracture plane, which is also the twin plane, and the sample surface is θ (or $90^\circ - \theta$), where θ is calculated by Eq. 5.1, as indicated in Fig. 5.1.

When the phase transformation is induced by varying the temperature, differently oriented martensite variants are introduced into the specimen after the martensitic transformation. These variants have to intersect and accommodate with each other, as shown in Fig. 5.8a. Otherwise, as illustrated in Fig. 5.7, microcrack may initiate on the habit plane of the barrier twin (the new created twin) and as a result, the crack plane is almost normal to the orientation of pre-existing twins. Fig. 5.10 shows a typical pattern of crack formed after about 100 thermal cycles. The crack propagated nearly parallel to the twin boundary of twin B, changed its orientation and stopped in twin C. It should be noted that the crack tip

closure occurred during the reversal transformation. However, microcrack may also initiate and propagate along the twin boundaries in each twin at different orientations. In this case, the angle between the crack planes is 2θ (or $180^\circ - 2\theta$) since both are on the $\{112\}$ planes, which is almost 90° , as shown in Fig. 5.11. This is a low magnification image comprised of about 30 micrographs connected together in which the cracks in different twin systems are connected to each other to form a network. It is obvious that once such crack network forms, a catastrophic failure may occur at any moment.

Figure 5.10. A typical observation of the crack formed in Ni-Mn-Ga single crystal as a result of thermal cycling. The crack propagated along the direction nearly parallel to the twin boundary of twin B, changed its orientation and stopped in twin C.[264]

Figure 5.11. Low magnification optical microscopic image showing the network of cracks formed due to thermal cycling in one polished surface ($3.96 \times 4.99 \text{ mm}^2$) of the Ni-Mn-Ga single crystal. [264]

To further investigate the effects of phase transformation on the crack propagation, a heating and cooling stage (TMS93, Linkam) was used to precisely control the temperature of the specimen during the optical microscopic observations. At room temperature, there were two pre-existing cracks (Fig. 5.12a) in the observed region. Nothing had changed in the surface morphology when the specimen was heated to below 44.9 °C. At this temperature, twin boundaries motion was observed as the traces of the twin bands began to drift, while the shape of the cracks did not change obviously (Fig. 5.12b). However, with further increasing the temperature, even by only 0.1°C, the crack 2 was found to heal up and the crack 1 was also narrowed (Fig. 5.12c). Further heating did not lead to any more change in either the crack or the morphology. During cooling, the cracks reopened at 39.9°C (Fig. 5.12e), and the variant boundaries began to move at 39.6°C (Fig. 5.12f).

Figure 5.12. Surface morphology change during one thermal cycle (RT → 60 °C → RT). The observations are schematically illustrated in sketch drawings in which the dash lines represent traces of the variant boundaries. See text for details. [48]

Fig. 5.13 shows that new twin system forms near the crack tip during crack propagation. A rapidly expanding crack has high shear stresses near the crack tip, producing a very high rate of stressing in the surrounding material. The large stress and high stress rate is likely to favor producing the deformation twins, such as in metals [210, 278, 282, 283] as well as shape memory alloys [284]. The new created twins have a strong influence on the fracture of a material, for example, acting as nucleation sites for new microcracks [278].

Figure 5.13. New twin system forms near the tip of a rapidly expanding crack.

Based on the observations, the crack propagation process during thermal cycling is suggested in Fig. 5.14. Once a crack is nucleated, it will self-propagate through opening-and-closure process during thermal cycles. The crack tip opens and closes with changing internal stresses related to the forward transformation and reverse transformation, respectively. It seems that the stresses built up during the forward transformation upon cooling and released during the reverse transformation. It is worth emphasizing that neither opening nor closure of the cracks takes place synchronously with the morphological change. There are small temperature intervals (0.1~0.3 °C) between the occurrences. During propagation of pre-existing cracks, new microcracks are nucleated nearly parallel to them (Fig. 5. 14a), due to the high stress concentration near the crack tips where dislocation density is high. Crack as small as ~1 µm with brittle cleavage character

were found in the SEM observations (Fig. 5.4c). Some deformation twins (Fig. 5.13 & 5.14b) seem to have formed near the advancing crack tip due to the high stress concentration. Branching (Fig. 5.3a) is another way for cracks to propagate. Growth of the branched cracks increases the probability of the crack interactions. Cracks propagated through different modes (as described above) with different orientations and connected to form a crack network, leading to easy fracture.

Some other factors may also affect the crack initiation and propagation procedure. Firstly, unlike the magnetostress, which is limited by the field strength or the magnetization saturation, the internal thermal stress can be higher with fast cooling. So according to Griffith's crack theory, increase of this internal stresses will result in loss of the fracture toughness. Besides, crack propagation will be accelerated by intersection between cracks of differently orientated martensite variants. If one martensite variant exists, the formation of a crack network is unlikely and the thermomechanical fatigue life may be improved. The brittleness of Ni-Mn-Ga due to thermal cycling is not an inherited property of thermoelastic transformation, since brittleness has never been observed in the various well-known SMAs having thermoelastic phase transformations like NiTi-base, Cu-base, etc. The fundamental reason for the brittleness frequently observed in the effects of Ni-Mn-Ga FSMAs is yet to be fully understood and further theoretical analysis on their thermally induced fatigue property are attempted in the next chapter.

Figure 5.14. (a) As suggested in the illustration, cracks formed and propagated along the twin-twin intersection region. (b) Deformation twins created near the crack tip due to the stress concentration. (c) A schematic shows the formation of the crack network by crack self-propagation and branch cooperation (the ellipses in dark color represent the main cracks, and shallow color ones branching cracks). [48]

5.3. Summary

In this chapter, the magneto-/thermo- mechanical fracture/fatigue behaviors of Ni-Mn-Ga FSMA have been investigated by monitoring the martensite morphologies of the surfaces and fracture planes.

Cracks initiation and propagation in Ni-Mn-Ga single crystal are much easier under thermal cycling through phase transformation temperatures. Crack initiation was considered as a result of twin dislocations pile-up along the twin boundaries. The cracks propagate not only along the twin variant boundaries, but also following the twin-twin intersections. High temperature rate weakens the fatigue property of Ni-Mn-Ga FSMA during thermal cycling. Several crack propagating modes are observed during thermal cycling, including opening-and-closure, branching, creation of new microcracks near the pre-existing crack tips and crack interactions. In situ optical observation shows that the opening-and-closure mode was strongly related to the phase transformation. Several pre-existing micro-cracks may finally develop into a crack network before catastrophic failure. Coexistence of differently oriented martensite variants was partially responsible for the poor fatigue property under thermal cycling.

Chapter 6 Effect of SIM transformation on the crack tip SIF in Ni-Mn-Ga SMAs

As described in chapter 2, it is generally accepted that the effect of SIM transformation in SMAs should be considered in order to understand their thermomechanical fatigue mechanism. Consequently, the crack tip SIF (K_I^*) consists of two contributions, one is due to externally applied load (K_I) and the other is due to localized phase transformation around the crack tip (K_{tr}) that redistributes the stresses, and can be expressed as $K_I^* = K_I + K_{tr}$. The SIM transformation results in an increase in the crack tip SIF when $K_{tr} > 0$, such as in NiTi SMAs, or an decrease when $K_{tr} < 0$ as in zirconia ceramics [285, 286]. One preliminary explanation [237, 254] was that the stress-induced martensite around the crack tip is surrounded by untransformed austenite; when there is a negative volume change, for instance a volume contraction of 0.5% in NiTi alloy [240, 255, 256], associated with the SIM transformation, an extra tensile stress field is created around the crack tip and it increases the crack tip SIF. It is thus suggested that the increase in crack tip SIF K_{tr} is strongly related to the magnitude of volume contraction. Finite element method (FEM) simulation [254] based on this argument shows that a 0.39% volume contraction results in an increase of the crack tip SIF for less than 12%.

Considering the much smaller volume contraction during martensitic transformation in Ni-Mn-Ga (in the order of 10^{-3} to 10^{-4} [287, 288]) than that in NiTi SMAs, it is

rather difficult to understand the much poorer thermomechanical fatigue property observed in Ni-Mn-Ga FSMA's if based solely on the above consideration. On the other hand, the volume change during the martensitic transformation is not necessarily to be negative. For example, a volume increase of $\Delta V/V = 0.5 \times 10^{-2}$ was reported in an equiatomic NiTi alloy [289]. Thus, in the present work, the effect of SIM transformation on the crack tip SIF is investigated through examining the stress redistribution in the region around the crack tip. As a result, the temperature dependence of crack tip SIF due to localized SIM transformation is established. The present results show that, in Ni-Mn-Ga FSMA's, the effect of volume contraction due to martensitic transformation on the crack tip SIF is less significant. The dominating factor is the localized SIM transformation taking place upon cooling to M_s that drastically increases the crack tip SIF through redistributing the local stresses. This is because of a decrease in the stresses applied on the region consisting of transformed martensites thus the additional stresses are counterbalanced with a change in the plastic zone size. In addition, the present report further discusses the factors that affect the temperature dependence of crack tip SIF and the effect of temperature rate of thermal cycling on the fatigue property of Ni-Mn-Ga FSMA's.

6.1. Theoretical Analysis

6.1.1 Mechanical behaviors of SMA

Typical stress-strain responses of SMA at three different temperatures are illustrated in Fig. 6.1. At temperature above M_d , the stress-strain curve is similar to that of a normal metal, with plastic deformation (via slip) commencing at a fairly low strain

amplitude. When the temperature is lowered (but still higher than M_s), SMA exhibits pseudoelastic behavior and the critical stress to induce martensite σ_{crit}^{SIM} decreases with decreasing temperature. When deformed isothermally, martensite volume fraction increases with increasing the strain within the stress plateau region [290]. To obtain complete pseudoelasticity, the deformation temperature should be higher than A_f . It is generally accepted that, starting from the end of the stress plateau, elastic deformation of stress-induced martensite takes place. Such martensite will yield at a higher stress level (σ_y^{SIM}) associated with dislocation processes. When the temperature is below M_s , thermally induced martensite appears and the phase transformation completes at M_f .

It is necessary to point out that the yield stress of the stress-induced martensite is temperature dependent. In a $Ti_{50}Ni_{50}$ thin film [291], the yield stress of both the stress-induced martensite and the thermally induced martensite decreases with increasing the temperature at a gradient of -0.7 MPa/K. However, the change in the yield stress is rather small if compared to its magnitude $\sigma_y^{SIM} \sim 1.3$ GPa [239, 292]. Thus, in the following analysis, the fluctuation of the yield stress within the temperature range of $M_s < T < M_d$ is ignored; σ_y is used to represent σ_y^{SIM} for simplicity.

Fig. 5.12 revealed that in Ni-Mn-Ga FSMA, microcracks propagate upon cooling and close up in the heating process. In the following, the effect of SIM transformation on the fracture toughness between M_d and M_s is examined. The analysis is performed on an infinite SMA plate containing a central crack subjected to an in-plane tensile stress

σ_0 perpendicular to the crack axis, thus is a typical mode-I fracture problem [293]. In the present analysis it is assumed that the external stress σ_0 is less than σ_{crit}^{SIM} at any temperature.

Figure 6.1. Illustration of typical stress-strain curves for (a) austenite, (b) stress-induced martensite, and (c) thermally formed martensite of SMAs. [279]

6.1.2 Plastic zone around the crack tip

According to the elastic-plastic fracture mechanics, a plastic zone always exists around the crack tip in ductile materials once there is an external (tensile) stress ($\sigma_0 > 0$). It is due to that, in a real material, the stress singularity at the crack tip predicted by the linear elastic fracture mechanics (LEFM) is relieved by yielding. The stress in the plastic zone is limited to yield strength σ_y , as schematically illustrated in Fig. 6.2 by the solid line. In this case, the stresses represented by the shaded area A

have to be carried by the material immediately ahead of the plastic zone so as to retain the equilibrium condition. As a result, the plastic zone expands and its size needs to be determined. One approach is the Irwin's plastic zone correction [294] in which the plastic zone size r_p is expressed as

$$r_p = 2r_{p1} = \frac{a \cdot \sigma_0^2}{\sigma_y^2} = \frac{(K_I^0)^2}{\pi \sigma_y^2} \approx \frac{K_I^2}{\pi \sigma_y^2} \quad (6.1)$$

where r_{p1} is the plastic zone radius calculated from the Irwin's first estimate, a the crack half-length, $K_I^0 = \sigma_0 \sqrt{\pi \cdot a}$ the stress intensity factor (SIF), and K_I is a correction to the SIF so that the plastic zone correction can apply consistently

$$K_I = \sigma_0 [\pi(a + r_p/2)]^{1/2} \quad (6.2)$$

As long as the crack half-length is much larger than the plastic zone size $a \gg r_p$, $K_I \approx K_I^0$. The geometric factor is ignored here. Combining the above two equations, both r_p and K_I are found to be functions of external stress σ_0

$$r_p = \frac{2\sigma_0^2}{2\sigma_y^2 - \sigma_0^2} a \quad (6.1a)$$

$$K_I = \sigma_0 \sqrt{\frac{2\pi \cdot a \cdot \sigma_y^2}{2\sigma_y^2 - \sigma_0^2}} \quad (6.2a)$$

Correspondingly, the stress field is given by,

$$\sigma = \begin{cases} \sigma_y & r < r_p \\ K_I / \left(2\pi \cdot (r - \frac{1}{2}r_p) \right)^{1/2} & r \geq r_p \end{cases} \quad (6.3)$$

where r is the distance from the crack tip. Using this approach, the LEFM keeps valid in the small-scale yielding (SSY) condition.

Figure 6.2. Illustration of elastic-plastic stress distribution ahead of a crack according to the Irwin's second estimate. A sharp tip only exists in the case of ideally brittle behavior. When the material is capable of plastic deformation, the sharp tip is blunted due to shearing and limited localized plastic deformation at the crack tip. [279]

At the temperature $M_s < T < M_d$, martensitic transformation is triggered around the crack tip in the area where the local stress is assumed to be higher than σ_{crit}^{SIM} according to Eq. 6.3. The stress-induced martensite region can be subdivided into two parts due to the asymptotic stress distribution along the crack propagation direction.

One consists of fully-transformed martensite and the other consists of partial martensite (the volume fraction of martensite $\xi < 1$). Thus, the area around the crack tip can be further divided into four regions as illustrated in Fig. 6.3. They are the plastically deformed detwinned martensite (I), elastically deformed detwinned martensite (II), stress-induced martensite (III) and (untransformed) austenite (IV), respectively, depending on the stress level. The stress is σ_y in region I, σ_{crit}^{SIM} in region III, and is linearly distributed in region II (proportional to the distance from the crack tip) indicating the elastic deformation of detwinned martensite. Beyond the

transformation zone, the stress field in region IV obeys Eq. 6.3. Comparing to the normal elastic-plastic stress distribution (dash line), it is rather similar to Fig. 6.2 that this piecewise-defined stress distribution results in a decrease in the load-bearing capacity (represented by the shaded area) of the crack plane. Thus, the equilibrium condition along the σ -direction is violated due to the SIM transformation and a redistribution of stress field around the crack tip is expected.

Figure 6.3. Illustration of four regions in front of a crack tip in Ni-Mn-Ga SMA at a temperature above M_s . They are the plastically deformed detwinned martensite, elastically deformed detwinned martensite, stress-induced martensite and austenite, respectively. The dimensions are denoted as r_p for the plastic zone, r_m for fully-transformed zone, and r_{tr} for whole transformation zone. Taking into account the difference in the microstructure and deformation status, the stress levels in these regions are expressed as a piecewise-defined function of distance from the crack tip, as illustrated by the curve 'a-b-c-d-e'. A redistribution of stress field around the crack tip is expected. [279]

6.1.3 Transformed zones

The martensite volume fraction ξ in the transformed zone increases up to 100% with decreasing the distance from the crack tip or with lowering the temperature to M_f^0 (the stress-free martensite finish temperature). According to the constitutive relation proposed by Tanaka et al. [295, 296], ξ is an exponential function of temperature (T) and effective stress (σ_{eff}),

$$\xi = 1.01 - \exp\{b_M(M_s^0 - T) + (b_M/d_M)\sigma_{eff}\} \quad (4)$$

where b_M is a material constant and is defined as $b_M = \ln 0.01 / (M_s^0 - M_f^0)$. When the material is in full martensite state $\xi = 1$ while in the parent phase $\xi = 0.01$. M_s^0 and M_f^0 are the stress-free martensite start and finish temperature, respectively. The parameter d_M defines the temperature dependence of the critical stress for SIM transformation, $\sigma_{crit}^{SIM} = d_m(T - M_s^0)$. For SMA with a given composition, d_M can be considered as a material constant. The effective stress is defined as the von Mises effective stress, and in the present problem, in the vicinity of crack tip where local stress dominates, it is equal to the stress given by Eq. 6.3 [293]. It is worth noting that the stress level in region III σ_{crit}^{SIM} is independent of ξ . The following analysis is to determine the transformed zone sizes r_m and r_{tr} .

It is deduced from Eq. 6.4 that the condition $\sigma_{eff} \geq d_m(T - M_f^0)$ is essential to obtain a fully-transformed zone ($\xi = 1$), which defines the boundary by combining with Eq. 6.3,

$$\mathbf{r}_m = \mathbf{K}_I^2 / \{2\pi \cdot d_M^2 (\mathbf{T} - \mathbf{M}_f^0)^2\} + 1/2 \mathbf{r}_p \quad (6.5)$$

It indicates that the fully-transformed zone expands at an increasing rate with lowering the temperature. Substituting Eq. 6.2a into Eq. 6.5, $\mathbf{r}_m$ can also be expressed as

$$\mathbf{r}_m = \frac{\sigma_0^2}{d_M^2 (\mathbf{T} - \mathbf{M}_f^0)^2} \cdot \frac{1}{2 - (\sigma_0/\sigma_y)^2} \mathbf{a} + \frac{1}{2} \mathbf{r}_p \quad (6a)$$

$$\text{or} \quad \mathbf{r}_m = \frac{\sigma_0^2}{(\sigma_{crit}^{SIM})^2} \cdot \left(\frac{\mathbf{T} - \mathbf{M}_s^0}{\mathbf{T} - \mathbf{M}_f^0} \right)^2 \cdot \frac{1}{2 - (\sigma_0/\sigma_y)^2} \mathbf{a} + \frac{1}{2} \mathbf{r}_p \quad (6.6b)$$

Combining Eq. 6.1a with Eq. 6.6b, the ratio of $\mathbf{r}_m$ to $\mathbf{r}_p$ is given

$$\frac{\mathbf{r}_m}{\mathbf{r}_p} = \frac{1}{2} \cdot \left(\frac{\sigma_y}{\sigma_{crit}^{SIM}} \right)^2 \left(\frac{\mathbf{T} - \mathbf{M}_s^0}{\mathbf{T} - \mathbf{M}_f^0} \right)^2 + \frac{1}{2} \quad (6.7)$$

The transformation zone size $\mathbf{r}_{tr}$ is determined as follows. The stress beyond the transformation zone obeys Eq. 6.3, and it will be equal to σ_{crit}^{SIM} at the boundary $\mathbf{r} = \mathbf{r}_{tr}$ if the stress distributes continuously along the crack propagation direction.

$$\sigma_{crit}^{SIM} = \mathbf{K}_I / \left(2\pi \cdot \left(\mathbf{r}_{tr} - \frac{1}{2} \mathbf{r}_p \right) \right)^{1/2} \quad (6.8)$$

It gives

$$\mathbf{r}_{tr} = \frac{\{\sigma_y^2 + (\sigma_{crit}^{SIM})^2\} \cdot \sigma_0^2}{(2\sigma_y^2 - \sigma_0^2) \cdot (\sigma_{crit}^{SIM})^2} \mathbf{a} \quad (6.9a)$$

if $\sigma_0 \ll \sigma_y$, then

$$r_{tr} \approx \frac{1}{2} \cdot \left\{ \frac{1}{(\sigma_{crit}^{SIM})^2} + \frac{1}{\sigma_y^2} \right\} \cdot \sigma_0^2 \cdot a \quad (6.9b)$$

Eq. 6.9b proves that the transformation zone is always wider than the plastic zone and it expands with lowering the temperature. Combining Eq. 6.6a and 6.9a, the region III consisting of partial martensite has a size of

$$r_{tr} - r_m = \frac{1}{2} \cdot \frac{\sigma_0^2}{d_M^2} \left\{ \frac{1}{(T - M_s^0)^2} - \frac{1}{(T - M_f^0)^2} \right\} a \quad (6.10)$$

6.1.4 Stress redistribution and its effect on SIF

The piecewise-defined stress distribution around the crack tip in Fig. 6.3 is unstable since there are some ‘additional stresses’ (the shaded area) need to be balanced. Thus, the plastic zone is expected to expand to carry these additional stresses and a stress redistribution is expected. The plastic zone size and the crack tip SIF after the stress redistribution are denoted as r_p^* and K_I^* , respectively. It is worth noted that the temperature does not change during this process. However, with lowering the temperature, fully-transformed zone expands (Eq. 6.5), and the other regions including the plastic zone will change accordingly.

Figure 6.4 schematically illustrates the stress redistribution around the crack tip after taking into account the SIM transformation. The same principle is followed, $\sigma = \sigma_y$ in the plastic zone (Region I'), $\sigma = \sigma_{crit}^{SIM}$ in the partial martensite zone (Region III'), and the stress distributes linearly in between these two regions. The remote stress field beyond the transformation zone obeys Eq. 6.3 is considered unaffected, thus r_{tr} does not change. Following the argument used in the Irwin's second estimate, the decrease

in load-bearing capacity in Region III' due to lowering the stress to σ_{crit}^{SIM} will be balanced by the increase in Regions I' and II'. More precisely, it is represented in Fig. 6.4 that the shaded regions A and B have the same area, thus the following equilibrium condition holds:

$$\int_{r_p}^{r_{tr}} (\sigma - \sigma_{crit}^{SIM}) dr = \frac{1}{2} (\sigma_y - \sigma_{crit}^{SIM}) \left\{ (r_p^* - r_p) + (r_m^* - r_p) \right\} \quad (6.11)$$

Assuming that the relation $r_p^* = (K_I^*)^2 / \pi \sigma_y^2$ is still applicable, the corresponding

fully-transformed zone size is $r_m^* = \frac{(K_I^*)^2}{2\pi \cdot d_m^2 (T - M_f^0)^2} + \frac{1}{2} r_p^*$. Then, Eq. 6.11 gives the

plastic zone size after the stress redistribution r_p^*

$$r_p^* = 2 \cdot \frac{\frac{\sigma_y}{\sigma_{crit}^{SIM}} \sqrt{\sigma_y^2 + (\sigma_{crit}^{SIM})^2} - (\sqrt{2} - 1) \sigma_y - \frac{\sigma_y^2 + (\sigma_{crit}^{SIM})^2}{2\sigma_{crit}^{SIM}}}{(\sigma_y - \sigma_{crit}^{SIM}) \left\{ \frac{3}{2} + \frac{\sigma_y^2}{d_m^2 (T - M_f^0)^2} \right\}} r_p \quad (6.12a)$$

Correspondingly,

$$K_I^* = \sqrt{2} \cdot \left(\frac{\frac{\sigma_y}{\sigma_{crit}^{SIM}} \sqrt{\sigma_y^2 + (\sigma_{crit}^{SIM})^2} - (\sqrt{2} - 1) \sigma_y - \frac{\sigma_y^2 + (\sigma_{crit}^{SIM})^2}{2\sigma_{crit}^{SIM}}}{(\sigma_y - \sigma_{crit}^{SIM}) \left\{ \frac{3}{2} + \frac{\sigma_y^2}{d_m^2 (T - M_f^0)^2} \right\}} \right)^{1/2} K_I \quad (6.12b)$$

It indicates that in SMAs, the effect of SIM transformation on the crack tip SIF

$K_{tr} = K_I^* - K_I$ is a function of temperature and (applied) SIF K_I (where σ_{crit}^{SIM} is also temperature dependent), but is independent of crack size a .

Figure 6.4. Illustration of stress field redistribution around the crack tip represented by the solid line, after taking into account the SIM transformation. To retain the load-bearing capacity, it is stipulated that area A is equal to area B. The dash line ‘a-b-c-d-e’ represents the normal elastic-plastic stress distribution. [279]

The transformation temperature range between which the above analysis is applicable needs to be redefined. Firstly, due to the stress effect on the M_s transformation temperature, the lowest temperature is changed to $M_s^0 + \sigma_0/d_m$. On the other hand, since σ_y is necessarily higher than σ_{crit}^{SIM} , the plastic zone must consist of complete martensite phase ($r_m \geq r_p$). From Eq. 6.6a, it deduces $\sigma_y/d_m + M_f^0 \geq T$. Thus, the temperature range $M_d > T > M_s$ is changed to $[T_1, T_2]$

$$T_1 = \sigma_y/d_m + M_f^0 \geq T \geq T_2 = M_s^0 + \sigma_0/d_m \quad (6.13)$$

It is assumed that there is no crack propagation upon cooling. Otherwise, the stress concentration around the crack tip is relaxed and the crack tip SIF is drastically

changed. In this case, the temperature range has to be changed to from T_I to the critical temperature when crack tip opens.

6.2. Results

Three types of SMAs, namely Ni-Mn-Ga, Ni-Ti and Cu-Al-Ni, are chosen to verify the effect of SIM transformation on the crack tip SIF (Eq. 6.12b). The software package Matlab is employed to create the following images. The materials properties used are listed in Table 6.1. Since only a few experiments have been carried out to measure d_M and yield stress σ_y simultaneously on the same specimen, thus, sometimes the σ_y data is collected from the experiments on the SMA with similar chemical compositions. This might result in some errors due to the composition dependence of material properties in SMAs. It is more difficult to determine the material properties of the Ni-Mn-Ga FSMAs. Firstly, few data on the yield stress of Ni-Mn-Ga single crystal were reported except it was briefly mentioned [297] that the plastic flow occurs at 200~350 MPa with no further details. Thus, an intermediate value of $\sigma_y = 300$ MPa is used in the following calculations. Secondly, d_m is influenced by many factors, such as the chemical composition, martensitic modulation ($5M$, $7M$ or NM), anisotropy, loading mode (tension vs. compression), etc. [62, 132, 190, 297, 298]. For example, it is 3.5 MPa/K along the $\langle 100 \rangle_c$ direction and 8.7 MPa/K along the $\langle 110 \rangle_c$ direction in a $\text{Ni}_{52}\text{Mn}_{24.4}\text{Ga}_{23.6}$ single crystal. Within the available results, the d_M values are in the wide range of 3.5~13 MPa/K for the $P \rightarrow 5M$ transformation. The effect of σ_y and d_M on the calculated results will be further

discussed in the next section. Transformation temperatures M_s^0 and M_f^0 are determined from DSC experimental results.

Table 6.1. Material properties of several types of SMAs used in the present numerical analysis. The critical temperature T_1 and T_2 are calculated using Eq. 6.13. (The chemical compositions are Ni₅₀Ti₅₀ in [292] and Cu-14Al-4Ni (wt.%) in [299]).

Alloy system	Chemical Composition	M_s^0 (°C)	M_f^0 (°C)	d_M (MPa/K)	σ_y (MPa)	T_1 (°C)	T_2 (°C)
Ni-Ti	Ni ₅₀ Ti ₅₀ [239]	-26.9	-54.8	6.4	1300	148	-26.9
	Ni _{50.2} Ti _{49.8} [300]	-12.2	-40.2	6.6	1250 [292]	149	-12.2
Cu-Al-Ni	Cu-14.0Al-4.2Ni wt.% [301]	34.8	22.8	2.04	780* [299]	405	35
	Cu-14.1Al-4Ni wt.% [302]	-31.2	-32.2	2.38		295	-31
Ni-Mn-Ga	Ni ₅₂ Mn _{24.4} Ga _{23.6} [62]	45.8	43	8.7	300	77.5	45.8
	Ni _{52.6} Mn _{23.5} Ga _{23.9} [137, 190]	19.8	9.8	13		32.9	19.8

Figure 6.5 shows the normalized transformation-induced SIF K_{tr}/K_I as a function of temperature in these SMAs, where $K_{tr} = K_I^* - K_I$ (thus K_{tr}/K_I is dimensionless). At high temperatures ($T \rightarrow T_1$), the crack tip SIF does not change much, but it increases quickly with further cooling. At the final stage ($T \rightarrow T_2$), a drastic increase in K_{tr}/K_I within a narrow temperature range exists in Ni-Mn-Ga and Ni-Ti SMAs,

as shown in Fig. 6.5a and 6.5b. This indicates that the effect of SIM transformation on the crack tip SIF is of the most significance when the temperature is close to M_s^0 . To some extent, it explains the observations in Figure 5.12 that microcracks propagate at the exact temperature 0.3 °C higher than M_s^0 . In the Ni-Ti SMAs, K_{tr}/K_I increases up to 0.4~0.5, which almost quantitatively coincides with the work of Holtz et al. [240] that the provisional fracture toughness K_Q was $\sim 65 \text{ MPa}\sqrt{m}$ at high temperature and $\sim 39 \text{ MPa}\sqrt{m}$ at low temperature ($T \rightarrow M_s$). They claimed that the provisional fracture toughness is not the valid plane strain fracture toughness value K_{IC} , but does reflect the actual SIF at which fracture takes place. As for the Ni-Mn-Ga FSMAs, in one case there is only a little change in K_{tr}/K_I with lowering the temperature, but in the other case SIM transformation causes a rather large increase (around three times) in the crack tip SIF. It indicates that Ni-Mn-Ga FSMAs can exhibit either stable or unstable fatigue resistance with changing the temperature, depending on the material properties, even though the material may be brittle in both conditions. It is interesting to note that there is a drop of K_{tr}/K_I in the midst of cooling process and this phenomenon is more obvious in the Cu-Al-Ni SMAs.

Figure 6.5. The temperature dependence of normalized SIM transformation-induced SIF in the (a) Ni-Mn-Ga, (b) Ni-Ti, and (c) Cu-Al-Ni SMAs, respectively. [279]

As presented in Fig. 6.5c, in Cu-Al-Ni SMAs, most calculated values of K_r/K_I are negative, suggesting that SIM transformation causes a decrease in the crack tip SIF with lowering the temperature. Thus, the fatigue property is improved. This result seems to be conflicting with previous understanding that SIM transformation will induce an increase in the crack tip SIF in Cu-Al-Ni SMAs [254, 303] since there is a volume contraction during the martensitic transformation. Furthermore, Experimental results obtained from polycrystalline Cu-Al-Ni SMAs [304] can not be used to support the argument since intergranular fracture occurs before martensites are stress-induced [305]. More recently, *in-situ* microscopic observations on Cu-Al-Ni SMA single crystal [306] found that the stress-induced martensite around a crack tip did not grow monotonically with increasing the load (or the applied SIF); instead, the fully-transformed zone shrinks not only upon unloading but also loading. As indicated by Eq. 6.7, the ratio between r_m and r_p is a constant in the isothermal condition.

Therefore, fluctuation in r_m reflects the change in the plastic zone size, and it has to be attributed to the stress redistribution around the crack tip.

The decrease in K_{II}/K_I with lowering the temperature is attributed to the region II' consisting of elastically deformed detwinned martensite. The stress in this region is a

function of distance from the crack tip, $\sigma_1 = \frac{r - r_p}{r_m - r_p} \sigma_y + \frac{r_m - r}{r_m - r_p} \sigma_{crit}^{SIM}$ according to

the piecewise-defined definition, or else $\sigma_2 = K_I / \left(2\pi \cdot \left(r - \frac{1}{2} r_p \right) \right)^{1/2}$ with the normal

elastic-plastic stress distribution, as shown in Fig. 6.3. The magnitude of σ_1 fluctuates with material properties and temperature thus may change the relation between σ_1 and σ_2 . Fig. 6.3 shows $\sigma_1 < \sigma_2$ throughout the transformation zone. However, it is possible that in certain SMAs, the relation $\sigma_1 > \sigma_2$ is obtained within certain temperature range in region II', i.e. along the distance 'b-x' in Fig. 6.6. Furthermore, if this distance increases to long enough with lowering the temperature, it is also possible that the stress redistribution results in an increase in the load-bearing capacity of the crack plane. In this condition, the equilibrium condition along the σ -direction can not be retained by plastic zone expansion. Instead, plastic zone has to shrink. The alternative postulation is that the sum of areas of A and C is equal to the area of B, as illustrated in Fig. 6.6. This requirement yields,

$$\int_{r_p}^{r_{tr}} (\sigma - \sigma_{crit}^{SIM}) dr + (\sigma_y - \sigma_{crit}^{SIM}) \cdot (r_p - r_p^*) = \frac{1}{2} (\sigma_y - \sigma_{crit}^{SIM}) (r_m^* - r_p^*) \quad (6.4)$$

which is mathematically equal to Eq. 6.11.

Figure 6.6. Illustration of stress distribution in the condition of plastic region shrinkage with lowering the temperature due to SIM transformation. It is stipulated that the sum area of shaded regions A and C is equal to that of B. [279]

6.3. Discussion

Equation 6.12b shows that the temperature dependence of normalized transformation-
Crack tip
induced SIF K_{tr}/K_I is affected by material properties of SMAs, i.e. σ_y , d_M , and transformation temperatures. Assuming a Ni-Mn-Ga single crystal with $M_s^0 = 19.8$ °C, $M_f^0 = 9.8$ °C, $d_M = 13$ MPa/K and $\sigma_y = 300$ MPa, the effect of changing these properties on the calculation results of K_{tr}/K_I is illustrated as follows. Remote applied stress σ_0 causes a shift of T_2 but does not influence the value of K_{tr}/K_I .

As shown in Fig. 6.7a, when the yield stress is in the range of 200~400 MPa, its effect on K_{tr}/K_I of Ni-Mn-Ga FSMA is negligible. The K_{tr}/K_I versus temperature curves nearly coincide with each other and the highest values of K_{tr}/K_I differ

slightly. However, if a high yield stress, e.g. 1000 MPa, is used in the calculation, the value of K_{tr}/K_I decreases significantly as shown in Fig. 6.7a. As further highlighted in the inset, at low temperatures, the value of K_{tr}/K_I is less than one third of the calculated values with $\sigma_y = 200\sim 400$ MPa. It can be succinctly explained that a higher yield stress leads to an increased shaded area in Fig. 6.4, thus increasing the stresses applied to the plastically deforming zone. Similar effect of d_M on the temperature dependence of K_{tr}/K_I is found, as shown in Fig. 6.7b where K_{tr}/K_I increases with increasing the d_M value at the same temperature.

Fig. 6.7c shows that transformation temperature $T_m = (M_s^0 + M_f^0)/2$ has no significant effect on the changing tendency of K_{tr}/K_I except that the curve shifts with different transformation temperatures. However, the transformation interval $(M_s^0 - M_f^0)$ has a much significant effect on the K_{tr}/K_I as shown in Fig. 6.7d. With increasing transformation interval, a much steeper increase in K_{tr}/K_I occurs upon cooling and the highest value of K_{tr}/K_I increases considerably. Further investigations indicate that either raising M_s^0 or lowering M_f^0 (fixing the other transformation temperature) results in an increase in K_{tr}/K_I .

Figure 6.7. The effect of (a) yield stress σ_y , (b) stress-transformation temperature gradient d_m , (c) transformation temperature $T_m = (M_s^0 + M_f^0)/2$, and (d) transformation interval $(M_s^0 - M_f^0)$ on the temperature dependence of normalized crack tip SIF K_{tr}/K_I . [279]

Experimentally determined transformation interval ($M_s^0 - M_f^0$) of Ni-Mn-Ga FSMAAs can be affected by the cooling rate. The TMA (Fig. 4.4) and DSC (Fig. 4.5) results have shown that the transformation interval increased with increasing the temperature rate, as indicated in Fig. 6.8. Thus, considering Fig. 6.7d, increasing the temperature rate will increase the crack tip SIF and weaken the fatigue property of Ni-Mn-Ga FSMAAs. This agrees well with the SEM observations on the same Ni-Mn-Ga alloy (Fig. 5.4) that crack initiation and propagation was found when the temperature rate was set at 5 °C/min.

Figure 6.8. DSC and TMA results (see section 4.1) show that transformation interval ($M_s - M_f$) is a function of temperature rate. [279]

6.4. Summary

The effect of SIM transformation on the crack tip SIF in the Ni-Mn-Ga FSMAAs is analyzed in the framework of elastic-plastic fracture mechanics and compared to NiTi and Cu-Al-Ni SMAAs. The results are summarized as follows.

1. Martensites are stress-induced in front of the crack tip in SMAs. The stress field around the crack tip is modified with the formation of martensite, leading to an increase in the crack tip SIF. With further lowering the temperature, the transformed zones expand and a change in the plastic zone size follows. As a result, the effect of SIM transformation on the crack tip SIF $K_{tr} = K_I^* - K_I$ is temperature dependent.
2. The effect of SIM transformation on crack tip SIF is verified in Ni-Mn-Ga, Ni-Ti, and Cu-Al-Ni SMAs. The normalized transformation-induced SIF K_{tr}/K_I is calculated as a function of temperature and shows significant differences. In Ni-Mn-Ga FSMA, the crack tip SIF increases more drastically when the temperature approaches to M_s .
3. The effect of SIM transformation on the crack tip SIF is strongly related to properties of SMAs. K_{tr}/K_I increases with decrease in the yield stress σ_y , increase in stress-transformation temperature gradient d_M and transformation interval $(M_s^0 - M_f^0)$.
4. SEM observations show that a high temperature rate can cause the initiation of crack and its propagation. Such phenomenon can be understood from the present analysis which shows that an increased transformation interval due to increased cooling rate will significantly increase the SIF of the crack tip in Ni-Mn-Ga FSMA.

Chapter 7 Summary and conclusions

In this research, thermomechanical properties and thermally-induced fracture of Ni-Mn-Ga FSMA single crystals were studied. The results from the experimental observations and theoretical analyses are summarized below.

Ni-Mn-Ga FSMAAs can exhibit irregularities in the two way memory effect (TWME) during stress-free thermal cycling. The shape memory strain of Ni-Mn-Ga FSMAAs can suddenly change from elongation to contraction or vice versa. Such irregularities in TWME are explained as a result of differently oriented twin variants redistribution, which is attributed to the internal stresses accumulated during thermal cycling. The accumulated internal stresses were calculated on the basis of M_s temperature change according to the modified Clausius-Clapeyron equation. The magnitude is comparable to the critical detwinning stress of Ni-Mn-Ga FSMAAs (1~3 MPa) thus is able to reorient the twin variants. For example, at the temperature rate of 5 °C/min, the internal stress accumulated within five cycles was about 1.4 MPa. Results further show that high temperature rate promotes the irregularity while applying a proper external load can help to stabilize the TWME.

Ni-Mn-Ga single crystals show poor fatigue property when being thermally cycled through phase transformation temperatures. The failure procedures of three Ni-Mn-Ga single crystals were studied by microscopic observations of the fracture surfaces. Results show that the cracks propagation behavior is strongly related to the {112} twin planes in martensite. Under thermal cycling, the cracks propagate along the

martensite variant boundaries through multiple modes, namely self-propagation (opening and closure), branching, new microcrack nucleation, and connection to form a network before catastrophic failure. On the other hand, thermal cycling introduces differently oriented twin systems. They meet at the domain boundary and result in twin-twin intersection. The mechanisms of dislocations pile-up and crack propagation along the intersection of different twin systems have been proposed. It was also noticed that during thermal cycling, the temperature rate plays an important role in the brittleness of Ni-Mn-Ga single crystal. For example, at the rate of 5 °C/min, microcrack with brittle cleavage character was found in the vicinity of a pre-existing crack.

The effect of SIM transformation on the crack tip SIF was further investigated to understand the thermally induced fracture property of Ni-Mn-Ga FSMA. The approach was to examine the stress redistribution around the crack tip. The area around the crack tip can be subdivided into four regions consisting of different microstructures and having different stress levels. The stress distribution around the crack tip in SMAs is a piecewise-defined function of the distance from crack tip, which is different from that in normal metals. It further causes changes in both the plastic zone size and the crack tip SIF. With lowering the temperature, the volume fraction of stress-induced martensite increases and the transformed zones expand, thus the plastic zone size varies accordingly to retain the stress equilibrium. Based on this argument, the crack tip SIF is expressed as a function of temperature and applied SIF. Results show that the crack tip SIF of Ni-Mn-Ga FSMA increases significantly with lowering the temperature to M_s , which is coincided with the *in situ* optical observations. Thus, crack propagation in Ni-Mn-Ga FSMA is strongly related to the

thermoelastic phase transformation. The temperature dependence of crack tip SIF is strongly affected by the yield stress, stress-transformation temperature gradient and transformation interval. High temperature rate under thermal cycling induces an increase in the transformation interval thus has very deleterious effect on the fracture behavior of the Ni-Mn-Ga FSMA.

Appendix A: Crystal structure of martensite

The crystal structural transitions during the martensitic transformation process have been investigated by various techniques in the past decade. However, the microstructure of Ni-Mn-Ga FSMAs is still to some extent confusing and conflicting. The following is a primary understanding of the martensitic structure unit cell according to the data published.

During the phase transformation, there is a necessary distortion of the martensitic lattice to determine the tetragonality. The experimentally observed orientation relationships are irrational due to the following distortion, which is schematically illustrated in Fig. A1 [35]. Upon transformation, the original structure of Ni-Mn-Ga compound changes from (a) cubic austenite to (b) tetragonal martensite. For the $5M$ structures, it is a compression along the z axis (or c -axis) and a uniform expansion along the x and y axes (a -axes). In (b), the atoms on one side of the indicated unit cell diagonal (representing one of the $\{110\}$ twin planes) are no longer mirror symmetric to their counterparts across it. A shift or shear deformation along the diagonal ($[\bar{1}01]$) is necessary to restore that symmetry. As a result (Fig. A1c), the structures on each side of the diagonal are twin variants of the same structure, and an extension dL is observed. The c - and a -axis of the sheared structure are rotated close to 90° away from their original orientations. Therefore, the variants 1 and 2 have almost perpendicular orientations, respectively.

Appendix A

Crystal structure of martensite

Figure A1. Scheme of the crystal structure transition during the martensitic transformation from (a) the ideal $L2_1$ Heusler alloy structure (a project along the $[010]_c$ direction) to (b) the transformed BCT (or FCT) martensite. With the shear deformation along the $\{110\}$ planes, the twinning related structures (c) are obtained.

In the follows, attentions are paid to the Bain corresponding referring to the martensitic transformation (Fig. A2), and the tetragonality schematized in Fig. A1 is ignored for simplicity. The basic martensitic structure (non-modulated) is described as a FCT unit cell, as indicated by the dash line in Fig. A2a. This structure is similar to the $L1_0$ martensite of Ni-Al alloys, but derived from the $L2_1$ ordered austenite instead of B2 [69].

The following orientation relations between the parent and produced lattices are obtained with $[001]_{fcc} // [001]_{bcc}$, $[1\bar{1}0]_{fcc} // [100]_{bcc}$ and $[110]_{fcc} // [010]_{bcc}$. Fig. A2b illustrates one of the six $\{110\}$ twinning plane, along which the shear deformation occurs. Obviously, the unit cell is not one-to-one corresponding with respect to the austenite.

However, it has been rather prevalent to choose the basic martensitic structure as a BCT unit cell, using the same coordination of the cubic $Fm\bar{3}m$ lattice (see the 2D schematic picture in Fig. 1). It consequently caused a conflict on the tetragonality with a ratio of

Appendix A

Crystal structure of martensite

$\sqrt{2}$, for example the lattice parameters $a \approx c$ in [134, 307] while $a \approx \sqrt{2} c$ in [69, 141, 188]. It further results in that, for example, the diffraction peaks with similar 2θ positions are referred to rather different crystal planes in the XRD patterns indexing between [134, 308], [123, 309, 310], [133, 307] and [69, 311]. On the other side, to avoid misunderstandings, authors had to use the cubic coordination to denote the directions in the martensitic phase. A consensus is expected to eliminate this fallibility and can be achieved technically by selecting the proper coordination.

Figure A2. (a) The lattice correspondence between the austenitic axes and those for the martensitic unit cell. There are six $\{110\}_c$ planes can be the twinning plane, and one is indicated by the shade area. It is shown in (b) that the twinning plane $(011)_A // (112)_M$ if different coordination are chosen.

The superlattice structures ($5M$, $7M$, or NM), treated as a derivation from the Heusler cubic by a periodic displacement of the atoms in successive (110) planes along the $[1-10]$ direction, are illustrated in [46, 69, 312]. As an example, the $5M$ structure with the periodic $(3\bar{2})_2$ sequence stacking of planes is presented (Fig. A3). The lattice parameters

Appendix A

Crystal structure of martensite

are $a = 4.24\text{\AA}$, $b = 5.66\text{\AA}$ and $c = 20.5\text{\AA}$, and the orientations is a along the $[1\bar{1}0]_c$ direction, b along $[001]_c$, and c along $[110]_c$. The fractional coordinates x_j of the positions of each j plane in the unit cell have been extracted from [46] (listed in the right table). Similar structures are found in other superlattices. The determination of lattice parameters in the superlattices is consistence in the literatures.

Figure A3. Unit cell corresponding to the $(3\bar{2})_2$ stacking sequence model of the $5M$ martensite with the lattice parameters $a = 0.424\text{ nm}$, $b = 0.566\text{ nm}$ and $c = 2.05\text{ nm}$.

Mn

Ga

Ni

Appendix B: Nanoindentation behaviors

Nanoindentation provides an accurate measurement on the continuous variation of indentation load, P , down to levels of micro-Newtons, as a function of the indenter penetration depth, h , down to levels of nanometers. The ability to deform a material at a small scale makes nanoindentation a useful tool for quantitative characterization of the mechanical properties, including the hardness and Young's modulus [313, 314]. When load is removed from the indenter, the material attempts to regain its original shape but it is prevented from doing so because of the plastic deformation. Only some degree of recovery happens with the relaxation of elastic strains. An analysis of the initial portion of this elastic unloading response gives an estimation of the elastic modulus of the indented material.

B.1. Elastic modulus and hardness

The indentation behaviors were investigated using a displacement-controlled Nano Indenter[®] XP system (MTS). Prior to testing, one surface was carefully polished (0.1 μm final polish) before gluing the specimen to an aluminum alloy holder. The nanoindentation process started at zero loads and displacement, but the indenter tip attaching to a standard diamond Berkovich indenter (apical angles 65.3°) gently touched the material's surface. Then increasing loads were applied to the indenter tip, forcing it to penetrate the sample surface until reaching the maximum depth, after which the load was

removed. This way, two indenter penetration depths were set, namely 3000 and 5000 nm. The surface approaching velocity was 5 nm/sec and the indentations were made at a constant nominal rate ($\dot{\epsilon} = \dot{P}/2P$) of 0.05 s^{-1} . The entire loading and unloading processes were recorded automatically by the machine. Since the indentation results were often influenced by unavoidable statistical variations, more than 5 locations were successfully tested for each penetration depth. All indentations were performed at room temperature under quasi-static loading conditions. After the experiments, the indentation impressions were examined by the SEM. Most measurement results were consistent.

A typical continuous load-unloading force-displacement curve for sample S-4 was plotted in Fig. B1. The initial deformation was likely elastic-plastic due to the high stress developed in a very small region under the sharp tip. For the two different penetration depths, 3000 nm and 5000 nm, these curves were similar in the aspect of the shape and the recovery ratio during unloading process. The inset illustrates the SEM image of penetration depth of 3000 nm. Though the depth limitation was set at 5000nm, the indentation tip stopped under 750 mN at about 3600 nm, implying a fully twinned microstructure [315]. The value was much less than that of a NiTi alloy, about 5N. The Young's modulus and hardness were calculated automatically from the load-displacement curves without imaging the indentations through the Oliver-Pharr method [316-318]. At the beginning of unloading process, they were 82.4 GPa and 3.0 GPa for the penetration depth 3000nm, and 85.7 GPa and 2.8 GPa for 5000nm (3600 nm), respectively.

Figure B1. Typical load–displacement curves of $\text{Ni}_{50.6}\text{Mn}_{28.2}\text{Ga}_{21.2}$ single crystal using a Berkovich indenter. The penetration depths were set at 3000 and 5000 nm, respectively.

The corresponding elastic modulus and hardness as a function of the penetration depth are also plotted in Fig. B2. The Young's modulus remained almost constant over the penetration depth, whereas the hardness decreased slowly and reached ~ 3 GPa at 1500 nm below the surface. The hardness change with depth may be attributed to the work hardening caused by mechanical polishing. The Young's modulus determined by nanoindentation (90~100 GPa) was significantly larger than that from the macroscopic stress-strain response during compressive and tensile loadings, 0.45~0.82 GPa [162]. A similar phenomenon was found in the NiTi SMAs that the elastic modulus was 101~162 GPa from nanoindentation experiments and 68 ± 5 GPa (or even lower) from macroscopic stress-strain curves [315, 319]. The difference has been attributed to that the strain is not obtained by a real elastic deformation, instead, there is twinning fraction in the

macroscopic strain. Using a strain gauge or an extensometer, it is difficult to distinguish the different contributions from elastic, twinning and plastic deformations. Therefore, the deformation at low stresses, which is expected to be largely elastic, may include twinning strain. This results in an artificially low elastic modulus, which is not truly representative of the elastic deformation [315]. Comparatively, Nanoindentation is theoretically not influenced by twinning. The hardness of Ni-Mn-Ga single crystal is in the same order with respect to the NiTi SMAs with a Vickers hardness 3.52 GPa [320, 321].

Figure B2. Elastic modulus and hardness as functions of penetration depth.

B.2. Pop-in events

Loading starts with an elastic deformation followed by an abrupt displacement increase at constant load, termed as “pop-in”, has been observed in different materials [322]. The cause of “pop-in” event may be generation and multiplication of dislocation loops in a single crystal [323], initiation of an irreversible deformation [324, 325], or cracking [313, 326]. It occurs only in the loading process. The characteristics of pop-in events depends on the parameter of the indentation experiments (e.g. hard or soft machine, tip radius,

loading rate) as well as the material properties (e.g. surface roughness, dislocation density, and crystallographic orientation).

Fig. B3.a shows a clear discontinuity in the P - h (set at 5000 nm) curve occurred during loading at the 350 mN load and about 3000 nm penetration depth. The displacement jump at this burst is about 750 nm, which is the longest among the available pop-in results in the SMAs. Obviously, this is the so-called “major pop-in” [327]. The major pop-in event took place once only, and the “minor pop-in” events occurred when pressed at other locations as can be seen in the inset.

As compared with typical load-displacement curve (dash line), both indentation load and penetration depth are drastically affected by the occurrence of the major pop-in event. At the beginning, the curves followed almost the same path. With increasing the indentation depth, the load on the indented spot lowered when there was a pop-in event, and the elastic modulus and hardness decreased simultaneously. There was a sharp drop of elastic modulus and a small jump of the hardness at the end of pop-in, as shown in Fig. B3.b and B3.c. After that, the elastic modulus and hardness values remained at a much lower level till the penetration depth reached at 5000 nm. The decrease in hardness and elastic modulus due to the pop-in events was also found in the ZnO single crystal [325] though the degree was much less. It was attributed to the different mechanisms of the pop-in events. In ZnO alloys, slip is the major plastic deformation mode and is considered as the cause of the pop-in event, while in the ‘brittle’ Ni-Mn-Ga FSMA, crack initiation at low loads [326, 328] is more likely the cause, considering the large displacement jump at the

burst. The other evidence is that when the major pop-in is induced by the generation of dislocation loops, after the pop-in the indentation load will increase rapidly, similar to the elastic loading [327]. But, in this experiment, the loading rate remained almost unchanged. However, it is clear that much additional work is required before a complete understanding of this phenomenon is obtained.

Appendix B

Nanoindentation behaviors

Figure B3. Major pop-in event and related characteristic change in elastic modulus and hardness. (a) the major pop-in with a displacement burst of ~ 750 nm at ~ 350 mN and the minor pop-in events (as indicated in the inset) found on other load-displacement curves. The dash line presents the nanoindentation behavior without pop-in events. The following are the corresponding hardness (b) and elastic modulus (c) as functions of penetration depth.

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