THERMOMECHANICAL TREATMENT OF Ni-Ti SHAPE MEMORY ALLOY

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Statement of Originality

The material in this thesis has not been submitted for any other degree at this or another institution. To the best of the author’s knowledge, this thesis contains no material previously published or written by another person, except where reference is made.

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Abstract

This study investigated the effects of thermomechanical treatments on the transformation and mechanical properties of NiTi alloys. Thermomechanical processing is an important technique for material production, shaping and property control of NiTi alloys. The effects of thermomechanical treatment have been one of the first focuses of research of NiTi alloys, yet in some areas the current knowledge is still incomplete or inadequate to enable predictive control and production of NiTi alloys and effective design of shape memory apparatuses.

The study investigated three main aspects of the influences of thermomechanical treatment on NiTi. Firstly, the effect of cold work percentage and partial anneal was studied to quantify the sensitivity of microstructural defects and imperfections toward thermal and mechanical behaviours of the alloy. Secondly, the influence and the mechanism of surface oxidation were analysed. The third topic was concerned with the creation of functionally graded NiTi by means of a novel gradient heat treatment technique.

Effect of cold work and partial anneal: The effect of cold work and partial anneal on the transformation and mechanical properties of near-equiaxial NiTi have been extensively studied and well reported in the literature. This work further advanced the knowledge by conducting a quantitative experimental study on (1) the influence of the percentage of cold work with respect to partial anneal temperature on the behaviour of Ti-50.5at%Ni alloy and (2) the effects of partial anneal on deformation induced martensite stabilisation. For a given anneal condition (temperature and time), the transformation temperatures were found to be suppressed and transformation stress increased as the percentage of cold work prior to anneal increased. Empirical analysis shows that the mechanical resistance that opposed the stress-induced transformation remained practically constant irrespective of the percentage of cold work for all the partial anneal temperatures. This implies that the increase of transformation stress was mainly caused by the suppression of the transformation temperatures, particularly that of B2→B19′. It is also found that partial anneal temperature influenced the amplitude of martensitic stabilisation effect significantly and that the stabilisation effect increased with increasing annealing temperature. A maximum magnitude of the stabilisation
effect of ~30 K was achieved from fully recrystallised samples and the minimum was practically zero for samples annealed at below 623 K. The two deformation modes of stress-induced martensitic transformation and martensite reorientation showed practically identical response to the deformation induced stabilisation effect.

Heat treatment induced oxidation and Ti depletion: Heat treatment in air causes oxidation of NiTi. Oxidation is found to occur by preferential leaching of Ti from the NiTi matrix, causing the formation of three distinctive layers on the surface and one Ti-depleted zone within the matrix. Low temperature and short exposure time in air caused the formation of a thin TiO$_2$ layer on the surface of NiTi, via a selective reaction of titanium with oxygen. Enrichment of Ni underneath the surface TiO$_2$ layer caused the formation of a second layer of TiNi$_3$. Prolonged exposure at high temperatures (above 873 K) induced further outward diffusion of Ti and inward diffusion of Ni, which led to the formation of a composite layer of TiO$_2$ and Ni(Ti) appearing in between the surface TiO$_2$ layer and the underneath TiNi$_3$ layer. Beneath the TiNi$_3$ layer in the matrix, there was also a region of depleted Ti, essentially enriching the matrix to be over rich with Ni. These surface layers exhibited no martensitic transformation, thus do not contribute to either the shape memory effect or the transformation latent heat measurement. The Ti-depleted zone may exhibit decreased transformation temperature in the region adjacent to the original matrix, but gradually loses its ability to transformation when the local Ni content increases to above a threshold toward the interface with the TiNi$_3$ layer, and act as a passive metal. These surface layers increased the mechanical resistance to stress induced martensitic transformation and hindered the recovery of shape change in pseudoelasticity. Removal of the surface layers restored the measurement of the latent heat of the transformation. Heat treatment in argon at temperatures above 1000 K was also found to cause depletion of Ti near the surface, despite of negligible oxide formed on its surface. The depletion depth increased as the heat treatment temperature and time increased. It is found that the thickness growth of the Ti-depleted layer from the treatment in argon was similar to the treatment in air. Correspondingly, the levels of critical stress to induce the martensitic transformation of these two treatment conditions were practically identical.

Functionally graded NiTi: This study explored a novel concept of functionally graded NiTi materials. Such materials are envisaged to exhibit gradually evolving properties from one section of a piece of the material to another. Such materials have the enhanced
ability to enable better control in actuation applications. This study explored the feasibility of creating functionally graded NiTi wires by means of gradient anneal and gradient ageing. It is found that gradient temperature anneal is effective in creating a piece of NiTi wire with varying deformation behaviour along its length, in particular with varying levels of the critical stress for inducing the martensitic transformation at a given temperature. The effective temperature range for gradient anneal for functionally graded Ti-50.5at%Ni was determined to be 600 – 800 K. The effective temperature range for functionally graded pseudoelastic Ti-50.5at%Ni was 630 – 783 K. Functionally graded NiTi created by gradient anneal exhibited unique “Lüders-type” deformation behaviour, with a positive “gradient stress plateau”. The stress interval achieved was 280 MPa for the stress-induced forward transformation and 300 MPa for the reverse transformation. The estimated plateau stress gradients for the stress-induced forward and reverse transformation were 4.7 GPa and 8.6 GPa, respectively. Gradient ageing was applied to Ti-50.8at%Ni. It is found that for 2 hours of exposure period, a good temperature range for gradient temperature ageing was 573 – 723 K. The stress interval achieved for the stress-induced forward transformation was 190 MPa, and the estimated plateau stress gradient was 2.5 GPa. In this regard, this novel heat treatment technique indicates a promising feasibility to improve controllability of near-equiaxed Ni-Ti alloys and expands the design possibilities of shape memory apparatuses.
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CHAPTER 1

SHAPE MEMORY ALLOYS AND THERMOELASTIC MARTENSITIC TRANSFORMATIONS

Shape memory alloys are a unique class of metal alloys which have the ability to return to their original shapes and dimensions after being deformed beyond the elastic limit. These alloys can sense and respond to external stimulations including heat, stress, pressure or magnetic field and exhibit mechanical actuation of large non-elastic but recoverable strains.

Owing to this unique and useful ability, shape memory alloys are considered smart and functional materials and have been made into a wide array of innovative applications, ranging from sensors, actuators, medical implants and apparatuses, to consumer gadgets, mechanical and aerospace components, and civil structures. Some of these applications improve the performances of the original technologies, some drastically simplify the complexity of design, and some create new opportunities and functions that are impossible without these alloys. Owing to their immense possibilities in application, shape memory alloys have attracted extensive interest in research and technological development in the past four decades especially since the discovery of the shape memory phenomenon in a Ti-55wt%Ni alloy in the early 1960’s [1]. The interest in adapting shape memory alloys in extended applications was further enhanced when the workability of Ni-Ti alloys was established [2].

To date, fundamental understandings on these alloys have been well established; meanwhile more technological developments and innovations are constantly produced. Crystallographic theories have been established comprehensively in explaining the phenomenon of diffusionless martensitic phase transformations and their lattice accommodation mechanisms [3-7]. Thermodynamic theories were established to
describe the thermomechanical behaviour of the martensitic transformations of these alloys [8-14]. Systematic studies have also been conducted to characterise the thermomechanical behaviour [15-19] and to investigate the effects of processing on the properties of these alloys, such as precipitation, alloy composition, cold work and anneal, and thermomechanical treatments [20-25]. In recent years, successful applications of shape memory alloys, particularly in medical technology and sensor-actuator related systems, have motivated more technology and application-based researches [26-29].

1.1 The Phenomenon of Shape Memory Effect

Shape memory effect refers to the phenomenon that a metal alloy reverts to its original shape upon heating after an initial deformation. Figure 1.1 shows an artist’s impression of the phenomena of the shape memory behaviour of a shape memory alloy. The initial shape of the alloy is straight. Upon the application of a bending load, the rod is deformed, as shown in (a), and the deformed shape remains upon the removal of the load, demonstrating that the deformation is non-elastic. When the bent rod is heated up to above a critical temperature, it reverts to its original shape instantaneously. This behaviour is known as the shape memory effect. By the same token, if the rod is deformed at an elevated temperature, above the critical temperature for shape recovery, the deformation will be recovered spontaneously upon unloading, as shown in (b). This is known as pseudoelasticity (or superelasticity, as referred to in some literature).

Whereas conventional metal alloys also exhibit various levels of deformation elasticity, shape memory alloys are far more superior in their much greater magnitudes of shape recovery. Spring steels may exhibit up to 0.5% recoverable elastic strain, whereas Ni-Ti shape memory alloys exhibit typically 5-8% recoverable strain, some 10 times greater. Additionally, the shape memory effect offers the rare opportunity to “store” the deformation and “delay” the shape recovery till heat is applied, whereas the pseudoelastic effect offers a superelastic deformation without the continuous increase of stress. Both characteristics have been well exploited in application.
1.2 The Mechanisms of Shape Memory Behaviour

Over the past several decades a wide range of shape memory alloys have been developed, ranging from Au-Cd, Cu-Zn, Cu-Al-Ni, Fe-Ti-Al to Ni-Ti and many more to list. These alloys differ widely with their chemical make-ups and crystal structures, and yet they all have one thing in common: they all exhibit macroscopic shape change via thermoelastic martensitic transformation. It has been established that these thermoelastic martensitic transformations are the fundamental mechanisms of the shape memory behaviour of shape memory alloys.

1.2.1 Thermoelastic Martensitic Transformation

Thermoelastic martensitic transformation is a diffusionless solid phase transformation, by which atoms move cooperatively, and often by a shear-like mechanism. This phenomenon is hypothetically illustrated in Figure 1.2(a). As a phase transformation, it involves crystal lattice change. Due to its cooperativeness and diffusionlessness, the lattice distortion at the unit cell level is accumulated and manifested into the shape change of the crystal. In this regard, a martensitic transformation is a mechanical deformation process microscopically as well as a phase transformation. In addition, this shape change is fully recoverable upon the reverse transformation and attributes towards
its shape memory effect and superelastic behaviour. In contrast, a diffusive solid phase transformation, as expressed in Figure 1.2(b), may exhibit a similar crystal lattice change, but the exterior shape of the whole crystal may remain unchanged. Therefore, it is clear that it is the combined effect of lattice distortion and diffusionlessness of the transformation that lays the foundation for transformation-related shape change of the materials, i.e. the shape memory effect.

![Hypothetical illustration to distinguish non-diffusion martensitic phase transformation](a) and diffusive phase transformation](b)

**1.2.2 Thermoelasticity of Martensitic Transformation**

A practical requirement for a martensitic transformation to exhibit shape memory effect is its reversibility. In this regard, various martensitic transformations are classified into two types, thermoelastic and non-thermoelastic transformations. Thermoelasticity of a martensitic transformation refers to the continuity and reversibility of the transformation process with respect to temperature changes. Such process may be described, in an abstract manner, as following. The transformation process continues with continued change of temperature, over a temperature interval, and reverses its direction when the sense of temperature variation is reversed, over a temperature hysteresis.

To achieve transformation continuity, the resistive force to the transformation needs to increase continuously, resulting in a continuous increase of the driving force for the transformation, i.e. continued cooling for the forward transformation or continued heating for the reverse transformation. To ensure reversibility, the resistive force against the transformation boundary movement must be small, i.e., the interface between the parent and the martensite must be highly mobile.

In contrast, if the interface between the parent and the martensite is immobile, the excessive resistive force, often caused by large transformation volume changes and
incoherent interfaces, may cause the transformation to proceed in a “burst” manner. In this case the transformation is regarded as non-thermoelastic. Due to the destruction of the transformation interfaces, there is no certainty of regaining the original crystal orientation and shape upon the reverse transformation, thus no shape memory effect. In some cases, the proper reverse transformation may be completely suppressed and replaced by non-martensitic transformations, like in the case of carbon steels in which the reverse process occurs by the decomposition of the martensite prior to reverting back to austenite.

1.2.3  **Self-Accommodation of Lattice Distortion**

In real polycrystalline materials, when we examine a grain in the interior of the material, it is clear that the grain is not permitted to change its shape freely. Therefore, the martensite has to negotiate its way to accommodate its lattice change into the same space of the parent phase. This happens by a mechanism known as “self-accommodation” of martensite variants. An essential condition for this to happen is that the parent and the product maintain a certain strict crystallographic relationship across the transformation interface to facilitate the diffusionless transfer of state of atoms from one structure to the other. This interface, inevitably an invariant plane between the two structures, is known as the habit plane and the crystallographic relationship is known as the lattice correspondence, as illustrated in Figure 1.3.

![Figure 1.3](image_url)  
Figure 1.3. Schematic illustration of (a) parent and martensite with invariant plane as habit plane [30] and (b) lattice distortion
Naturally, the parent phase is having a high symmetry crystal structure whereas the martensite phase is of a lower symmetry. This enables the martensite to form into multiple variants along the habit plane, and thus accommodates the lattice distortion to be contained within the grain boundaries. All these conditions make the transformation fully reversible, by which the lattice correspondence dictates the reverse path of the product phase to only a single variant of the parent phase. Figure 1.4(a) schematically illustrates the shear-like lattice change during the transformation in which the atoms organise themselves to accommodate the lattice distortion within the grain boundary limit. The collective movement of atoms in such a manner produces relief on the free surface of the alloy, which can be physically viewed using optical microscopes. Figure 1.4(b) shows an optical micrograph of the surface relief of martensite in a Ni-Ti single crystal alloy [31].

![Schematic illustration and optical micrograph of surface relief](image)

Figure 1.4. Self-accommodation of martensite in near-equiatomic Ni-Ti (a) schematic illustration and (b) optical micrograph of surface relief [31]

### 1.2.4 Stress-Induced Martensitic Transformation

As discussed above, a thermoelastic martensitic transformation is also a mechanical deformation process. Therefore, it is possible to induce the transformation by the application of a stress, as is by the variation of temperature. In this case, the material yields a deformation in the direction of the applied stress. Owing to the nature that martensite may form in multiple variants in a number of different directions, the transformation may be induced by an applied stress in any direction. The only criterion is that the applied stress must be sufficient to overcome internal resistances to the phase transformation and at the same time below the yield strength of the matrix, otherwise plastic deformation will take place. This mechanism allows the structure to accumulate
the lattice changes to align toward an outmost single direction and subsequently produces a global strain, as shown in Figure 1.5 for a near-equiatomic Ni-Ti alloy.

![Figure 1.5. Stress-strain curve illustrating the accumulation of lattice changes from the stress-induced transformation that produces a global strain](image)

**1.3 Thermodynamics of Thermoelastic Martensitic Transformation**

Thermoelastic martensitic transformation is a mechanical process as well as a phase transformation. As a phase transformation, it is responsive to change of temperature, and as a mechanical process, it is responsive to stress variation. This renders the transformation unique thermodynamic characteristics. Fundamental thermodynamic theories have been established [8-14] to describe these unique characteristics and to express the laws governing the behaviour, as discussed below.

**1.3.1 Temperature-Stress Equivalence as Driving Force for Thermoelastic Martensitic Transformations**

To express the effect of an applied stress on the equilibrium condition of the transformation, Wollants et al. [8-10] examined a system as shown in Figure 1.6. The body is under a uniaxial load $F$ and produces an elongation $\Delta L$ when undergoing the transformation. Under this condition, the free energy balance of the system during the transformation can be expressed as:

$$
\Delta G = \Delta H - T \Delta S - F \Delta L = \Delta H - T \Delta S - \frac{1}{\rho} \sigma \epsilon
$$

(1.1)
The changes of enthalpy energy ($\Delta H$) and entropy energy ($T\Delta S$) express the chemical free energy contribution, which originates from the lattice change of the transformation. The term $F\Delta L$ expresses the mechanical contribution, i.e. the mechanical work done to the system. $V$ and $\rho$ are the specific volume and density of the material respectively, $\sigma$ is the external applied stress and $\varepsilon_t$ is the strain associated with the transformation. Differentiating the equation under the equilibrium condition ($\Delta G=0$, $T=T_o$ and $\sigma=\sigma_o$) gives:

$$\frac{d\sigma_o}{dT_o} = \frac{-\rho\Delta S}{\varepsilon_t} = \frac{-\rho \Delta H}{T_o \varepsilon_t}$$

This equation is famously known as the Clausius-Clapeyron relation [8, 9], which defines the relationship between the equilibrium stress and equilibrium temperature as the driving forces for the transformation. Given that all parameters on the right hand side of the equation are constants for a given transformation system, this equation defines a linear relationship between $T_o$ and $\sigma_o$. This linear relationship has been well confirmed experimentally, as shown in Figure 1.7 [32].
Non-steady State Conditions of Thermodynamic Relation

The previous section discussed about the effect of a constant applied stress on the equilibrium condition of the transformation. Under this condition the transformation takes place at one specific temperature dependent on the stress. In reality, at least for polycrystalline materials, it is commonly believed that an internal elastic stress is continuously created and accumulated during the process of the transformation [11-13]. This defines a non-steady state condition in which the stress changes continuously.

The cause of this internal elastic stress is believed to be the lattice distortion of the transformation, thus the state of the internal stress is expected to be dependent on the configuration and the volume fraction of the martensite variants formed [33-36], though this has never been properly verified experimentally.

In thermodynamic context, this phenomenon is expressed as elastic stress-strain energy of the matrix, \( \Delta E_{\text{el}} = \frac{1}{2} \sigma_{\text{el}} \varepsilon_{\text{el}} \). This energy is continuously stored during the forward
transformation and released during the reverse transformation, i.e. $\Delta E_{el}^{\text{rev}} = -\Delta E_{el}^{\text{fwd}}$.

This effect manifests as continuously changing transformation temperatures, known as transformation intervals.

### 1.3.3 Non-equilibrium Contributions of Thermodynamic Relation

In addition to the various reversible contributions, the actual process of a thermoelastic martensitic transformation also involves non-reversible energies, collectively expressed as $\Delta E_{ir}$. These include the energies consumed in creating internal defects, emission of acoustic waves and generation of heat [37-39]. The occurrence of these events causes the transformation to depart from its equilibrium path, for both the forward and the reverse processes. This phenomenon manifests as transformation hysteresis.

### 1.3.4 Phenomenological Theory Thermodynamics of Thermoelastic Martensite

Summarising the contributions of both the elastic energy ($\Delta E_{el}$) and the irreversible energy ($\Delta E_{ir}$), Ortin and Planes [11] and Salzbrenner and Cohen [13] proposed the following free energy equation to describe the process of thermoelastic martensitic transformations:

$$\Delta G = \Delta H - T\Delta S + \Delta E_{el} + \Delta E_{ir}$$  \hspace{1cm} (1.3)

This equation allows the description of the phenomenon of a transformation hysteretic loop, including the hysteresis and transformation intervals by proper treatment of the elastic and irreversible energy terms. In practice, the irreversible energy is often regarded as a constant during the process of a transformation and takes the same sign (as energy consumption) for both the forward and the reverse transformations, thus being responsible for the hysteresis. The elastic energy is often regarded to continuously increase during the forward transformation and decrease during the reverse transformation, thus being responsible for the transformation intervals. The effects of $\Delta E_{el}$ and $\Delta E_{ir}$ are schematically shown in Figure 1.8, together with that of the $\frac{1}{\rho}\sigma e_i$ term for comparison.
Figure 1.8. Schematic illustration of the effect of elastic and irreversible energies on transformation behaviour: (a) $\frac{1}{\rho} \sigma \varepsilon$, (b) $\Delta E_{el}$ and (c) $\Delta E_{ir}$.

Equation 1.3 has been widely used in the literature. However, its interpretation has much been erroneous, in particular with respect to the definition of the elastic and irreversible terms. The free energy equation (Equation 1.3) expresses the free energy balance at a particular moment during the process of the transformation (note: not the equilibrium state because of the inclusion of the irreversible term). It is irrelevant to the transformation processes before or after that moment. Therefore, it is explicit that all the terms in the equation are specific quantities corresponding to an infinitesimal step of the transformation, but not cumulative energy quantities over a certain period of the transformation. In this regard, the elastic and irreversible energies properly and exactly expressed as

$$\Delta E_{el}(f_m) = \frac{dE_{el}}{df_m}$$

and

$$\Delta E_{ir}(f_m) = \frac{dE_{ir}}{df_m},$$

i.e. the rates of generation of the elastic and irreversible energies at a moment corresponding to $f_m$ during the course of the transformation. This concept has been heavily misunderstood in the literature to date. The integral of these specific energies with respect to the volume fraction of martensite yields the total cumulative quantities over the transformation, as:

$$E_{el} = \int_0^{f_m} \Delta E_{el}(f_m)$$

(1.4a)

$$E_{ir} = \int_0^{f_m} \Delta E_{ir}(f_m)$$

(1.4b)

These relationships can be schematically illustrated as shown in Figure 1.9, where $\Delta E_{el}(f_m)$ is assumed a linear function of $f_m$ and $\Delta E_{ir}(f_m)$ is assumed constant during the process of transformation. As discussed earlier, two thermodynamic equations have been established to describe the process of thermoelastic martensitic transformations. These two equations describe different aspects of the transformations. Equation (1.1) describes the equilibrium and steady state condition of the transformation whereas
equation (1.3) describes the shape of the transformation hysteresis loop. The combination of these two equations thus describes the full aspects of the transformation:

$$
\Delta G = \Delta H - T \Delta S - \frac{1}{\rho} \sigma_i \varepsilon_i + \Delta E_{el}(f_m) + \Delta E_{ir}(f_m)
$$

(1.5)

Figure 1.9. Schematic illustration of internal energy entities during martensitic transformation: (a) stress-strain elastic energy and (b) irreversible energy [40]

1.3.5 Determination of Thermodynamics Parameters

Due to the involvement of the irreversible energy, the forward \((fwd)\) and the reverse \((rev)\) transformations occur at different temperatures. Therefore, to express the transformation temperatures, equation (1.5) is split into two separate equations as [11]:

A\(\rightarrow\)M: \(\Delta G^{fwd} = \Delta H^{fwd} - T \Delta S^{fwd} - \frac{1}{\rho} \sigma_i^{fwd} \varepsilon_i^{fwd} + \Delta E_{el}(f_m)^{fwd} + \Delta E_{ir}^{fwd}(f_m)\) (1.6a)

M\(\rightarrow\)A: \(\Delta G^{rev} = \Delta H^{rev} - T \Delta S^{rev} - \frac{1}{\rho} \sigma_i^{rev} \varepsilon_i^{rev} + \Delta E_{el}(f_m)^{rev} + \Delta E_{ir}^{rev}(f_m)\) (1.6b)

The enthalpy and entropy used in these equations are state functions. Therefore, \(\Delta H\) and \(\Delta S\) are equal in magnitude and opposite in sign for the forward and reverse transformations, as expressed in equation (1.7). Since the forward transformation is exothermic, \(\Delta H\) and \(\Delta S\) on the forward transformation are treated as negative.

$$
\Delta H^{fwd} = -\Delta H^{rev} < 0
$$

(1.7a)

$$
\Delta S^{fwd} = -\Delta S^{rev} < 0
$$

(1.7b)
Under the condition that the transformation does not produce plastic deformation and the transformation strain induced on the forward transformation is fully recovered on the reverse transformation, the magnitude of transformation strain on the forward and reverse are equal and treated as:

\[ \varepsilon_f^{\text{fwd}} = -\varepsilon_f^{\text{rev}} \tag{1.8} \]

Similarly, as the elastic stress-strain energy is stored in the system on the forward transformation and released on the reverse transformation, therefore:

\[ \Delta E_{el}^{\text{fwd}} (f_m) = -\Delta E_{el}^{\text{rev}} (f_m) > 0 \tag{1.9} \]

Lastly, the irreversible energy is considered as a consumption of the free energy driving force and is physically determined by the actual transformation path and metallurgical matrix condition. Under the assumption that the transformation paths are equal on the forward and reverse, and the matrix is unchanged, this energy may be treated as equal, thus:

\[ \Delta E_{ir}^{\text{fwd}} (f_m) = \Delta E_{ir}^{\text{rev}} (f_m) > 0 \tag{1.10} \]

With all these conditions, the transformation temperatures of a thermally induced transformation, where the external stress of \( \sigma = 0 \), can be determined from equation (1.6), when the change of the free energy \( \Delta G = 0 \). Therefore:

\[ T^{\text{fwd}} (f_m) = \frac{\Delta H^{\text{fwd}} + \Delta E_{el}^{\text{fwd}} (f_m) + \Delta E_{ir}^{\text{fwd}} (f_m)}{\Delta S^{\text{fwd}}} \tag{1.11a} \]

\[ T^{\text{rev}} (f_m) = \frac{\Delta H^{\text{rev}} + \Delta E_{el}^{\text{rev}} (f_m) + \Delta E_{ir}^{\text{rev}} (f_m)}{\Delta S^{\text{rev}}} \tag{1.11b} \]

and

\[ M_s = T^{\text{fwd}} (0) \tag{1.12a} \]

\[ M_f = T^{\text{fwd}} (1) \tag{1.12b} \]

\[ A_s = T^{\text{rev}} (1) \tag{1.12c} \]

\[ A_f = T^{\text{rev}} (0) \tag{1.12d} \]
Following the definitions of equations (1.11) and (1.12), the temperature intervals for the forward and reverse transformations can also be calculated as:

\[
\Delta T^{\text{fwd}} = M_s - M_f = \left[ \frac{\Delta E_{el}^{\text{fwd}}(0) - \Delta E_{el}^{\text{fwd}}(1)}{\Delta S} \right] + \left[ \frac{\Delta E_{ir}^{\text{fwd}}(0) - \Delta E_{ir}^{\text{fwd}}(1)}{\Delta S} \right] \tag{1.13a}
\]

\[
\Delta T^{\text{rev}} = A_f - A_s = \left[ \frac{\Delta E_{el}^{\text{rev}}(0) - \Delta E_{el}^{\text{rev}}(1)}{\Delta S} \right] + \left[ \frac{\Delta E_{ir}^{\text{rev}}(0) - \Delta E_{ir}^{\text{rev}}(1)}{\Delta S} \right] \tag{1.13b}
\]

The transformation hysteresis can be determined using the equation (1.11), as:

\[
\eta_T = T^{\text{rev}}(f_m) - T^{\text{fwd}}(f_m) = \frac{2 \times |\Delta E_{ir}^{\text{fwd}}(f_m)|}{\Delta S} \tag{1.14}
\]

Equation (1.11) illustrates that the transformation temperatures are influenced by the amount of the elastic stress-strain energy and the irreversible energy. Equation (1.13) illustrates that the transformation temperature interval is determined by the differences between the starting values and the finishing values of the specific elastic stress-strain and the irreversible energies of the transformation. Equation (1.14) indicates that the transformation hysteresis is caused by involvement of irreversible energy during the transformation.

1.4 Thermomechanical Behaviours of Thermoelastic Martensitic Transformation

As discussed above, a thermoelastic martensitic transformation is a mechanical process as well as a phase transformation, and thus is responsive to stimulations of both temperature and stress. Therefore, a thermoelastic martensitic transformation may exhibit different thermal and mechanical behaviours under different testing temperature. In addition, it may also exhibit complex behaviour under the influences of internal microstructure variations and alloy composition.

1.4.1 Thermal Transformation Behaviour

Thermoelastic martensitic transformations are easily detected by means of differential scanning calorimetry (DSC), internal friction method and electrical resistance technique, with DSC being the most commonly used. Figure 1.10 shows an example of
thermal transformation behaviour of fully annealed near-equiaatomic Ni-Ti, as detected by DSC. The transformation on cooling is exothermic and the reverse transformation on heating is endothermic. The transformations occur with a thermal hysteresis of typically ~30 K and latent heat of ~25 J/g on both cooling and heating. From such measurement, the following transformation parameters are conventionally defined:

- **Ms**: starting temperature for the forward austenite (B2) → martensite (B19’) transformation.
- **Mf**: finishing temperature for the forward austenite → martensite transformation.
- **As**: starting temperature for the reverse martensite → austenite transformation.
- **Af**: finishing temperature for the reverse martensite → austenite transformation.
- **ηAM**: thermal hysteresis of the martensite ↔ austenite transformation.
- **ΔT_{fwd}**: temperature interval of the forward transformation.
- **ΔT_{rev}**: temperature interval of the reverse transformation.
- **Δh**: heat change during transformation as determined by the area covered under the thermal peak in the spectrum.

![Diagram of Thermal Transformation Behaviour](image)

**Figure 1.10.** Thermal transformation behaviour of near-equiaatomic NiTi

### 1.4.2 Mechanical Behaviour

Figure 1.11 demonstrates typical tensile deformation behaviour of a near-equiaatomic polycrystalline Ni-Ti alloy. At that testing temperature, the alloy is initially in austenite...
phase. The deformation behaviour may be divided into four stages. The early stage deformation proceeds with apparent linear elasticity, labelled Stage I. This stage is the elastic deformation of the austenite. The stress plateau in Stage II commencing at $\sigma_{\text{cri}}$, corresponds to the stress-induced $A\rightarrow M$ transformation. The critical stress of Stage II is a function of temperature [32], as expected for the need to compensate for chemical free energy deficit to induce the transformation at $T>M_s$. In Stage III the stress continues to increase rapidly again with increasing strain, but with an apparent nonlinearity. This simulates a mixed deformation of elasticity and plasticity of the transformed martensite, and in addition further production of transformation strain [41-43]. Stage IV is the plastic deformation of the stress-induced martensite upon passing the yield strength of the alloy, $\sigma_y$. Unloading at this stage leaves a residual strain. The residual strain includes transformation strain, $\varepsilon_{\text{re}}$, (which may be recovered upon heating), and permanent plastic strain, $\varepsilon_{\text{pl}}$.

![Graph showing tensile deformation behaviour of NiTi shape memory alloy](image-url)

Figure 1.11. Tensile deformation behaviour of NiTi shape memory alloy

### 1.4.3 Thermomechanical Behaviour

Deformation behaviour of shape memory alloys is governed by deformation temperature. Figure 1.12 demonstrates this temperature-dependence of shape memory behaviour in Ni-Ti alloy. Thermal transformation behaviour as measured by DSC is inserted in the plot to provide temperature reference for the tests.
The deformation behaviour may be divided into three different types based on the testing temperature, including (a) pseudoelastic behaviour (PE), (b) shape memory effect (SME) and (c) martensite reorientation (MR). In addition to these behaviours, a simultaneous forth and back shape changes by cooling and heating is also possible in the absence of external mechanical force, as shown in (d). This behaviour is known as the two-way memory effect (TWME).

1.4.3.1 Pseudoelastic Behaviour

Pseudoelastic (PE) behaviour refers to the spontaneous recovery of large inelastic deformation upon unloading at a constant temperature, as shown in (a) in Figure 1.12. The deformation is completely recoverable, thus “elastic”, yet the deformation does not follow the classic Hooke’s law of elasticity, thus “pseudoelastic”. It occurs by the mechanism of stress-induced martensitic transformation upon loading and the reverse transformation upon unloading. Therefore, complete pseudoelasticity can only occur at deformation temperatures above \( A_f \). The critical stress to induce the transformation increases as the testing temperature increases, following the Clausius-Clapeyron relation [8, 9, 44, 45].
1.4.3.2 **Shape Memory Effect**

When deformed at below the $A_s$ temperature, the deformed martensite will not revert back to austenite spontaneously when the external stress is removed, leaving a residual strain. The residual strain may be recovered upon heating after unloading. This is the shape memory effect (SME), as shown in (b) in Figure 1.12. Deformation at $T<A_s$ may be achieved via either stress-induced martensitic transformation or martensite reorientation, depending on the starting structure. In practice, shape memory effect is most easily realised in materials of ideal crystals, or in engineering terms, fully annealed, neutral matrix of large grains [17-19, 46-48].

1.4.3.3 **Martensite Reorientation**

This deformation behaviour occurs when the alloy is deformed at $T_3$, a temperature below $M_f$. At this temperature the alloy is in martensite state and an applied load reorientates the martensite variants via twin boundary movement to align with the direction of the stress. Typically, the critical stress for martensite reorientation is lower than the stress-induced transformation, owing to the high mobility of coherent twin boundaries. This stress is also temperature-insensitive [30-32], because that martensite reorientation is merely a mechanical process and involves no phase transformation, thus does not obey the Clausius-Clapeyron relation.

1.4.3.4 **Two-Way Shape Memory**

Two-way memory effect refers to the spontaneous forth and back shape changes during heating and cooling, without the interference of a mechanical force. Two-way memory effect is not an inherent property of the transformation. It requires prior “training” of the material to exhibit such behaviour. The training may be a simple deformation or repeated deformation-heating cycles under a bias load [41, 49-51]. It is generally regarded that TWME arises due to the influences of anisotropic internal stress fields, which may be created by directionally organised dislocation arrays or retained martensite from prior thermomechanical training [52-56]. These directional internal stress fields promote the formation and growth of a preferentially oriented martensite upon cooling, very much in the same manner as an externally applied stress. TWME has been found to amount to more than 5% strain by means of careful thermomechanical
cycling training for NiTi [41] and ~4.3% as a result of a simple uniaxial tensile deformation via martensite reorientation [51].

1.4.3.5 *Ferroelastic Behaviour*

In the martensitic state, a shape memory alloy may also be deformed forth and back repeatedly by the application of an alternative reverse load, producing a ferromagnetic-like deformation hysteresis loop, as shown in Figure 1.13(a). This behaviour is referred to as ferroelasticity [57]. The area enclosed within a ferroelastic hysteretic loop corresponds to the mechanical energy dissipated during the deformation cycle. Given that the deformation cycle involves no plasticity, or dislocation movement, ferroelastic deformation experiences minimum hardening and fatigue effect and thus promises good potential for cavitations resistance and damping applications [58-60]. For comparison, a symmetrical pseudoelastic behaviour induced by alternative reverse loading at above $A_f$ is also shown in the Figure 1.13 (b).

![Figure 1.13. Ferroelasticity: (a) deformation via martensite reorientation and (b) pseudoelastic deformation via stress-induced martensitic transformation](image)

1.4.3.6 *Rubber-Like Behaviour*

Rubber-like behaviour is another unique behaviour of shape memory alloys arising from the effect of martensite ageing. This behaviour has been found in Au-Cd, Au-Cu-Zn, Cu-Zn-Al, Cu-Al-Ni and In-Ti [20, 61]. It refers to the spontaneous reversible deformation of the martensite, in a manner similar to pseudoelastic deformation, as depicted in Figure 1.14. In this case no stress-induced phase transformation is involved but only the reorientation and restoration of the martensite variants. This behaviour
stems from a general tendency of the symmetry of short-range ordering configuration of point defects in the detwinned martensite [61].

Figure 1.14: Rubber-like deformation behaviour of Au-47.5at%Cd after ageing in martensitic state [20]

1.5 Shape Memory Alloys

The first shape memory alloy discovered was Au-Cd in 1932 by Olander [62]. The discoveries of other alloys were only intensified after the successful adaptation of NiTi alloy in navy engineering application [2]. Since then, as the interest and technology emerge, and motivated by the demand in many potential applications, more than 50 different alloy systems have been discovered. Table 1.1 lists some examples of shape memory alloys and their corresponding lattice structures in the austenite and martensite phases. These alloys can be divided into three main categories, based on their response to external stimulation for phase transformation: thermal, magnetic and electrical.

Thermal shape memory alloys are the most established category and are commonly subdivided in types according to their base element in the alloy system. Among all thermal shape alloys, Ni-Ti is the best candidates for applications due to its excellent shape memory properties, good mechanical properties and high corrosion resistance. Magnetic shape memory alloys are attractive for their ability to change their shape in response to magnetic field. They are also best known for their ability to produce large transformation strain at high frequency response, in the kHz regime [63], and at one order of magnitude higher than magnetostrictive materials [63-65].
Table 1.1. A list of available alloys exhibiting shape memory behaviour via thermoelastic martensitic transformation [19, 64-67, 69-72]

<table>
<thead>
<tr>
<th>Alloy Group</th>
<th>Alloy System</th>
<th>Composition (at%)</th>
<th>Crystal Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Austenite</td>
<td>Martensite</td>
</tr>
<tr>
<td>Rare-element</td>
<td>Ag-Cd</td>
<td>44-49 Cd</td>
<td>B2</td>
</tr>
<tr>
<td></td>
<td>Au-Cd</td>
<td>46.5-48 Cd</td>
<td>B2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49-50 Cd</td>
<td>B2</td>
</tr>
<tr>
<td>Copper-based</td>
<td>Cu-Zn</td>
<td>38.5-41.5 Zn</td>
<td>B2</td>
</tr>
<tr>
<td></td>
<td>Cu-Zn-X</td>
<td>38.5-41.5 Zn</td>
<td>B2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a few at% X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu-Al-Ni</td>
<td>28-29 Al</td>
<td>DO3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0-4.5 Ni</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu-Sn</td>
<td>~15 Sn</td>
<td>DO3</td>
</tr>
<tr>
<td></td>
<td>Cu-Au-Zn</td>
<td>23-28 Au</td>
<td>Heusler</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45-47 Zn</td>
<td></td>
</tr>
<tr>
<td>Ni-Ti-based</td>
<td>Ni-Al</td>
<td>36-38 Al</td>
<td>B2</td>
</tr>
<tr>
<td></td>
<td>Ti-Ni</td>
<td>49-52 Ni</td>
<td>B2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B2 - R (trigonal) - B19’</td>
</tr>
<tr>
<td></td>
<td>Ni-Ti-Cu</td>
<td>8-20 Cu</td>
<td>B2</td>
</tr>
<tr>
<td></td>
<td>Ti-Pd-Ni</td>
<td>0-40 Ni</td>
<td>B2</td>
</tr>
<tr>
<td>Iron-based</td>
<td>Fe-Pt</td>
<td>~25 Pt</td>
<td>ordered FCC</td>
</tr>
<tr>
<td></td>
<td>Fe-Pd</td>
<td>~30 Pd</td>
<td>disordered FCC</td>
</tr>
<tr>
<td></td>
<td>Fe-Ni-Co-Ti</td>
<td>33 Ni, 10 Co, 4 Ti</td>
<td>disordered FCC</td>
</tr>
<tr>
<td>Magnetic</td>
<td>Ni-Mn-Ga</td>
<td>~24-28 Mn</td>
<td>Heusler cubic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~21-25 Ga</td>
<td>L2₁</td>
</tr>
<tr>
<td></td>
<td>Mn-As</td>
<td>~50:50</td>
<td>Hexagonal B8₁</td>
</tr>
<tr>
<td></td>
<td>Ni-Mn-Al</td>
<td>~53:25:22</td>
<td>L2₁</td>
</tr>
<tr>
<td></td>
<td>Co-Ni-Al</td>
<td>~27-34 Ni</td>
<td>B2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~27-29 Al</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe-Pd</td>
<td>~30 Pd</td>
<td>Cubic A1</td>
</tr>
<tr>
<td></td>
<td>Fe₃Pt</td>
<td>3:1</td>
<td>ordered L1₂</td>
</tr>
<tr>
<td>Electrical (ferroic)</td>
<td>BaTiO₃</td>
<td>1:1:3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Pb,Sr)TiO₃</td>
<td>8 Pb, 12 Sr</td>
<td></td>
</tr>
</tbody>
</table>
Electro-shape-memory alloys simulate the piezoelectric effect, by which reversible shape actuation is induced by electrical field. In addition, these alloys could produce up to 0.185% of strain [66, 67], which is more than 10 times of strain achieved in most piezoelectrics [68].

Most shape memory materials are metal alloys. Some ferromagnetic shape memory materials have the characteristics of intermetallic compounds [64]. Shape memory phenomenon is also observed in ceramics, such as lead zirconate titanate Pb(Zr,Ti)O$_3$ [73] and CeO$_2$-stabilised tetragonal zirconia (ZrO$_2$) polycrystals [74]. Shape memory behaviour is also observed in certain polymeric materials [75]; however the mechanism is completely different from that in metal alloys. A typical example of shape memory polymer is represented by rubber.

1.6 Applications of Shape Memory Alloys

Innovations of shape memory alloy applications are dramatic, as relative to the period in which they were discovered. In less than half of a century, countless number of new and replacement designs have been developed and produced [29], most remarkably in the medical and sensor-actuator markets. In most cases, the design and mechanism of the applications utilise mainly the shape memory effect and pseudoelasticity of the alloys. The choice of shape memory alloys over other mechanisms is mainly motivated by their design simplicity for compatible functions.

1.6.1 Medical Apparatuses and Implants

Applications of shape memory alloys are more popular and successful in the medical and dental markets. Typical applications include surgery apparatuses and implants, such as flexible puncture needles, flexible biopsy forceps, coronary dilatators, brain spatula, hingeless grasper, stone retrieval basket, stents, bone plate and orthodontal wire. Most of these devices utilise pseudoelastic effect of the alloys, by which the device may be shrunk and kept in compact confinement to enable minimal invasive surgery operations. Once the device is positioned at the intended site it is released from the confinement and its full shape is resumed. In some other applications the shape memory effect is utilised. In this case the shape recovery is achieved by a simple heating to a moderate temperature that will not damage the human tissue. Figure 1.15 shows a few examples.
of the mentioned devices. The flexible needle, as shown in (a), is used in interventional radiology for therapeutic treatment of slipped disc diagnosis. The hook is initially withdrawn into the thin tube and deployed into the site in the body, then pushed out of the tube to resume its hook shapes by pseudoelastic effect. The tip of the needle could then be easily positioned to target the particular spot or angle. This design allows surgeons/radiologists to easily access suspected tissue areas and lymph and bypass specific anatomic obstacles such as bones and spine, or vital structure such as organ, larger vessels and nerves.

A SMA marrow needle is shown in (b). It provides compressive force on the broken thigh bone once the intended shape of the plate is regained by heating. This compressive stress helps to heal the fracture faster. The insertion process of the needle is greatly improved by using the shape memory alloy. Figure 1.15 (c) illustrates the use of stents in treating blockage or narrowing of blood vessel or heart valve. Traditionally stents have been constructed from stainless steel and due to the large movement of the vessel wall it may fail to remain dilated. However, SMA stent offers a self-expanding mechanism via pseudoelastic behaviour, where the shape is always retained even if the vessel experiences squeezing or twisting. It also provides a constant force over a large expansion diameter against the vessel wall, therefore minimises the possibility of vessel burst or collapse if the fluid pressure changes.

Figure 1.15. Shape memory alloys in medical apparatuses and implants; (a) flexible tissue ablation device [26], (b) marrow needle [76] and (c) stent [26]
Among all available shape memory alloys used in this area of application, NiTi is mostly used due to its biocompatibility. Also, NiTi alloys show a good compatibility to magnet resonance imaging (MRI) and therefore can be used directly without causing much adverse effect. Additionally, NiTi shape memory alloys also exhibit very similar deformation behaviours to a few human body components such as hair, bone and tendon, as shown in Figure 1.16.

![Comparison of mechanical tensile behaviours](image)

Figure 1.16. Comparison of mechanical tensile behaviours [27]

1.6.2 Engineering Devices and Components

The earliest and most well-known large scale engineering application of SMA is in the U.S. defence where a coupling was used to connect titanium hydraulic tubing in the F-14 air-craft. SMA alloys won the selection over other conventional techniques when the need for reliability and weight saving were the priority. Following this success, more similar mechanism-related devices were invented including electrical connectors, fastener and weld reinforcement. In principle, these devices work by utilising the transformation stress generated from shape recovery of the alloys. An example of a coupling is shown in Figure 1.17, in which the tubing ends are jointed by a simple and single piece device that contracts to provide a high compressive stress upon heating. The main advantages of this mechanism are its lightweight as compared to other screw-type couplings, easy installation even in difficult areas of access, proven reliability, and good shock, vibration and thermal cycling resistance.
Recently SMAs continue to explore their functionality in commercial aircraft [28], typically as hingeless mechanisms in wings and chevron for achieving optimum airflow. Here the alloys are integrated in complex mechanism and their role is as an active material to actuate the main components by their shape recovery through heating. Figure 1.18 shows an example of this application on engine chevron, mainly to reduce the noise from the air-jet flow during take off.

Shape memory alloys are also used as sensor-actuator devices. Conventional actuation mechanisms are normally constructed from piezoelectric ceramics, magnetostrictive materials and electrorheological and magnetorheological fluids. Their actuations are generally stimulated and controlled by independent sensing devices. Conventional sensing mechanisms are commonly achieved from optical fibres, piezoelectric materials and microelectromechanical systems. In contrast, shape memory alloys respond to input signal as a sensor and spontaneously provoke actuation at the predetermined displacement or force. Even though wax actuator and bimetallic elements do sense
temperature and produce actuation, shape memory alloys are able to deliver much larger force and displacement and the response time is far quicker than wax. These combined functions make shape memory alloys deployed over conventional actuators such as electromagnetic solenoids, pneumatic or hydraulic devices and electric motors. Additionally, shape memory actuators can be designed without friction mechanism, which makes it free from friction particle and vibration and therefore the movement occurs in silence. Although acoustic emission is produced by the martensitic transformation, it can only be detected by special detectors and completely well below the human hearing range. Also, shape memory actuator can be designed to work without using high-current or electrical switch for heating, which makes it spark-free operation and therefore desired in highly inflammable environments. Finally, shape memory alloy actuators can work in tension, compression, bending, shear or rotation, making them robust and versatile.

Figure 1.19 shows a shape memory actuation mechanism for a water mixing valve. When the mixed water is too hot, the shape memory spring activates and pushes core piece of the valve to the right to reduce the inflow of hot water. When the mixed water is too cold, the shape memory spring softens and the bias spring pushes the core back to the left to allow more hot water to enter the flow.

Shape memory alloys are also used as dampers for vibration control in engineering and civil structure. This property makes the alloys more superior in term of fatigue-resistance, high damping capacity, large recoverable displacement and stable behaviour as compared to dampers made of viscoelastic materials and low yield strength metals,
mostly polymer based [58]. The application on structure control can be classified into three categories: passive control, active frequency tuning and active damage control [60]. The passive control utilises the damping capacity of the SMA via martensite reorientation and stress-induced transformation mechanisms. These enable it to dissipate vibration energy of structures subjected to dynamic loading [79]. A typical design is schematically illustrated in Figure 1.20 where connector rods are used to provide damping and to tolerate relatively large deformations in steel structures caused by earthquakes. Active frequency control is used for tuning the resonant frequency of the structures. The operation is achieved by embedding SMA actuators in the structure, by which upon heating the actuators contract and increase the stiffness of the host structures, and subsequently the natural frequency of the structures can be actively tuned [80]. Active damage control is developed to self-rehabilitate macro-size cracks in concretes or compensate large structure movement. SMA wires or beams are embedded in concrete and are allowed to contract upon the growth of crack via its pseudoelastic property or by electrical heating of the shape memory effect alloys [81]. Although the use of SMA in engineering structures is relatively new, it indicates a huge potential of market demand for bulk materials of these alloys.

![Figure 1.20. SMA connector for steel structure [82]](image)

### 1.6.3 Miniature Devices

Recently development has seen the advance of these alloys into micro-components miniature devices [83-88]. Figure 1.21 illustrates the simplicity of the shape memory effect gripping mechanism at micron level by which the constant gripping force is maintained by electrical heating [89]. The use of SMAs in miniature devices is largely encouraged by the fact that conventional actuators are difficult to scale down in size specifically considering friction forces between parts and the complexity of design. In
comparison, SMAs are self-actuating and involve no friction between different parts. SMAs also have the highest power/weight ratio among all known actuators.

One drawback of the shape memory actuator in miniaturisation is that it requires materials in extremely small dimensions, typically within the 10s of microns, and less than 5 microns of thickness for thin film. This requirement imposes a technological challenge on the production of shape memory alloys with much smaller grain size, possibly within the nano-scale, in order to be genuinely polycrystalline and isotropic. Many efforts have been reported for microstructure refinement using several techniques, such as thin films [90-93], ribbons [94-96] and severe plastic deformation of bulk material [97-100].

![Miniature SMA devices](image)

(a) Figure 1.21. Miniature SMA devices: (1) microgrippers holding an optical fibre of 140 μm diameter [89] and (b) fabrication of SMA microgrippers [101]
CHAPTER 2

Ni-Ti SHAPE MEMORY ALLOYS

2.1 Metallurgy of Ni-Ti

Binary near equiatomic Ni-Ti alloys are conventionally produced by melting and casting in controlled environment, either in vacuum or in inert gas due to the high reactivity of titanium with oxygen. The alloys also have excellent workability suited for most conventional processing techniques. Final shapes are normally achieved by forging, rolling, tube extrusion and wire drawing. Cold drawing and forming are also customised to alter their shape memory properties for specific applications. In many cases, these alloys are also subsequently heat treated either for annealing or ageing to enhance their shape memory properties.

2.1.1 Phase Diagram

Figure 2.1 shows the current understanding of the phase diagram of this alloy system, as published by Massalski [101]. In the original phase diagram there were a dotted lines at 1090°C implying a BCC↔B2 order-disorder transition and another one at 630°C indicating a eutectoid decomposition of the B2-NiTi phase into Ti$_2$Ni and TiNi$_3$. With vast amount of experimental evidences and many discussions, these lines have been removed from the phase diagram [102, 103].

As mentioned in Chapter 1, the shape memory property of this alloy system is only achieved from the near-equatomic TiNi phase, with a very tight atomic composition tolerance, by which the typical range reported is between 49.5at% to 51.5at% of nickel. This can be easily understood from the phase diagram that the TiNi phase is only represented by a vertical line at temperature below ~630°C. The boundary of the TiNi phase region on the Ti-rich side is nearly vertical, indicating a very low variation of the solubility of titanium in TiNi. In this regard, any excessive titanium in the matrix will
exist in the formation of Ti$_2$Ni. In contrast, on the Ni-rich side, the nickel solubility in TiNi increases as the temperature increases from above 630°C and reaches the maximum solubility of ~57at% at 1118°C. This allows the near-equatomic TiNi phase to exist in a wider range of composition with excessive nickel in the matrix. This condition can facilitate diffusional precipitation transformation to form some Ni-rich phases, including Ti$_3$Ni$_4$, Ti$_2$Ni$_3$ and TiNi$_3$, via ageing treatment. In practice, single-phase TiNi is achievable via solidification from the liquid state.

![Phase diagram of Ni-Ti alloy](image)

**Figure 2.1. Phase diagram of Ni-Ti alloy [101]**

### 2.1.2 Diffusional Phase Transformations of the B2 Phase

Due to the variation of the solubilities of nickel and titanium in NiTi, the NiTi phase experiences some precipitation transformations via diffusion. The NiTi phase has an ordered CsCl type structure, thus demands an ideal atomic composition of 50-50. Deviation from such stoichiometry is expected to produce precipitates under proper conditions.

Precipitation reactions have been found in both Ti-rich [104] and Ni-rich alloys [102], with the Ni-rich alloys attracting most attention. The precipitation process of Ni-rich
alloys during ageing treatment is summarised in the TTT (time-temperature-transformation) diagram shown in Figure 2.2 (a) [102]. As seen in the diagram, ageing at lower temperatures and for shorter times produces Ti$_{111}$Ni$_{14}$ phase (which is later identified as Ti$_3$Ni$_4$ [105]). Increasing ageing temperature and time leads to the formation of Ti$_2$Ni$_3$. At higher temperatures and for even longer times, TiNi$_3$ is formed. Among these precipitate phases, Ti$_3$Ni$_4$ and Ti$_2$Ni$_3$ are metastable forms and TiNi$_3$ is the stable phase. This sequential diffusional transformation can be summarised in the following order with increasing ageing time and temperature:

$$\text{Ti}_3\text{Ni}_4 \rightarrow \text{Ti}_2\text{Ni}_3 \rightarrow \text{TiNi}_3$$

The stable TiNi$_3$ phase is usually formed only in binary Ni-Ti alloys of excessively high nickel contents outside the normal composition range for shape memory effect. Therefore, from a practical point of view, it is also useful to express the metastable phase equilibria in the phase diagram, shown in Figure 2.2 (b) for the Ti$_3$Ni$_4$ phase [30]. As seen in this diagram, the solubility of Ni in the TiNi phase at equilibrium with Ti$_3$Ni$_4$ is slightly greater than that with TiNi$_3$. This knowledge is useful and critical in designing ageing-related heat treatment to optimise the shape memory properties of the alloys. The Ti$_2$Ni$_3$ boundary is not reported in the literature, largely due to the nature that its existence does not contribute much advantage to shape memory properties.

![Figure 2.2. Precipitate evolution in binary NiTi: (a) TTT diagram for precipitation transformation process for Ti-52at%Ni [102] and (b) metastable precipitation phase diagram [30]](image-url)
It is only the coherent Ti$_3$Ni$_4$ precipitate that interacts with the martensitic transformation. Ti$_3$Ni$_4$ precipitate appears to be thin lenticular in shape, as shown in Figure 2.3 (a). It has a trigonal structure. The unit cell is composed of six layers with an additional nickel atom occupying a titanium atom position on every second layer, thus containing 18 titanium atoms and 24 nickel atoms (Ti:Ni ratio = 3:4) [106]. Its growth habit in the B2 matrix is (001)$_T$//(111)$_{B2}$, making the (001)$_T$ planes to stack along the [111]$_{B2}$ direction, as shown in Figure 2.3 (b). This close relation of crystal structures and the coherency of the interface minimises the disruption of structure continuity between the precipitate and the B2 matrix. The slight mismatch of the lattice parameters aside the coherent interface produces stress-strain fields around the precipitates, causing some degrees of lattice distortions to the matrix and the precipitate itself. These lattice distortions and stress-strain fields play the role in altering the thermal transformation behaviours and in affecting the shape memory effect and pseudoelasticity [107-110]. In addition, this precipitate is also an important element in developing the two-way shape memory effect [49, 111, 112].

![Figure 2.3. Ti$_3$Ni$_4$ precipitates; (a) TEM micrographs showing the precipitate structure from Ti-51.5at%Ni [113] and (b) schematic illustration of lattice distortion surrounding the precipitate [114]](image)

2.1.3 Crystal Structures and Martensitic Transformations of the B2 Phase

The near equiatomic NiTi may exist in three distinctive phases, the parent phase (also known as the austenite), the martensite and the R-phase. The parent phase has a cubic B2 (CsCl) type structure with a lattice constant of 0.3015 nm at room temperature, for Ti-49.75%Ni [115]. This lattice constant varies slightly as the composition changes.
This effect is more obvious on the Ni-rich side because of the higher solubility of Ni in the TiNi matrix. A schematic illustration of this B2 structure is shown in Figure 2.4 (a). The martensite phase has a monoclinic B19’ structure, as shown in Figure 2.4 (b). This structure is transformed from the parent B2 phase by a large cooperative shear-like lattice distortion on the (001)_{B2} plane along the [110]_{B2} direction. On the other hand, R-phase is an intermediate phase that may be transformed between B2 and B19’, when the alloy is subjected to mechanical or thermal treatments and addition of third alloying element. The structure of this phase may be illustrated by stretching the parent lattice along the [111]_{B2} diagonal direction, as shown in Figure 2.4 (c). Therefore, it may be viewed as a rhombohedral lattice distortion of the B2, making it to be initially reported in the literature to have a rhombohedral structure, thus the name “R”, but later determined to be trigonal [116].

![Figure 2.4. The crystal structures of NiTi alloys; (a) cubic parent B2 structure, (b) monoclinic B19’ martensite structure [117] and (c) trigonal R-phase structure [118]](image)

Among these three phases there exist three possible martensitic transformations: B2↔B19’, B2↔R and R↔B19’. All these transformations are thermoelastic in nature. Since the transformations involve lattice distortion, structural defects are also introduced to the microstructure during the process of transformation. This phenomenon deteriorates the reversibility of the transformation and demotes the stability of its functional property. Among these three transformations, B2↔B19’ and R↔B19’ are characterized by large lattice distortions and large transformation hystereses. In contrast, lattice distortion and transformation hysteresis of B2↔R are very small. This implies lesser damage to the microstructure during transformation as compared to B2↔B19’ and R↔B19’ transformations. This advantage makes the B2↔R transformation to be more profound in application that requires high cycle stability.
2.2 Thermomechanical Behaviour of NiTi

Thermodynamic status of the parent B2 phase depends sensitively on the degree of ordering, hence stoichiometry of chemical composition and perfection of microstructure of the alloy matrix. Consequently, transformation behaviour and thermomechanical properties of NiTi are strongly affected by thermomechanical treatment and alloy composition.

2.2.1 Thermal Transformation Behaviour

As discussed above, near-equiaxial NiTi shape memory alloys may exhibit three possible thermoelastic martensitic transformations among the three phases. Under solution treated and fully annealed condition, near-equiaxial Ni-Ti alloys undergoes a single-step $B2 \leftrightarrow B19'$ transformation. Figure 2.5 (a) shows DSC measurement of a single-step transformation in a Ti-50.5at%Ni alloy, with the exothermic and endothermic peaks manifesting the first order nature of the transformation. The transformation occurs over a temperature window of around ~10 K, referred to as the transformation interval ($\Delta T$) and with a hysteresis of ~30 K ($\eta$) between the forward and the reverse processes. However, this transformation sequence changes when the microstructure of the alloy is altered, such as via cold-work and partial anneal, as shown in figures (b) and (c). It is known that the recrystallisation temperature for this alloy is ~850 K [15]. Annealing at 773 K, as shown in (b) has caused the forward transformation to proceed in two-step transformations of $B2 \rightarrow R$ and $R \rightarrow B19'$. Meanwhile, the reverse transformation shows only a single-step transformation of $B19' \rightarrow B2$. As the annealing temperature is lowered to 723 K, as shown in (c), caused the reverse transformation also to proceed in two step of $B19' \rightarrow R$ and $R \rightarrow B2$. Additionally, R-phase transformation may also appear when the alloy microstructure is altered by ageing precipitation [119-121], thermal cycling [122-124] and addition of a third element [125-128].
The asymmetric transformation sequence shown in Figure 2.5 has been explained in thermodynamics expression [16], as shown in Figure 2.6. With the assumptions that the entropies of all phases remain constant within the temperature range of concern, the free energies of the phases are expressed as linear functions of temperature, according to equation 2.1.

\[ G = H - TS \] (2.1)

When the system involves only entropy and enthalpy changes, the transformation proceeds at \( T_0 \) where \( G^{B2} = G^{B19'} \) (for the case of \( B2 \leftrightarrow B19' \) transformation). However, when the transformation also experiences frictional resistance, the transformation actually occurs at:

\[ T^{B2-B19'} \quad \text{for } B2 \rightarrow B19' \]
\[ T^{B19'-B2} \quad \text{for } B19' \rightarrow B2 \]

The separation of the forward and the reverse processes of the transformation creates a hysteresis in between. To express this effect of the frictional resistance to
transformation, or the occurrence of hysteresis, the free energy state of one of the two transforming phases, B19’ for example, may be expressed using two parallel lines [16], one for the forward transformation (B19’+) and the other for the reverse transformation (B19’-), as shown in Figure 2.6 (a). For the same argument, the free energy state of the R phase may also be expressed using two parallel lines. The separation of the two lines expresses the magnitude of the hysteresis [16, 129]. Given the fact that the thermal hysteresis of the B2-R phase transformation is much smaller than that of the B2-B19’ transformation, the split of the free energy line for the R phase is much narrower.

In this expression, the system always takes the lowest free energy state at any given temperature. For the situation shown in (a), the transformation occurs in a single step B2→B19’ at \( T^{B2-B19'} \) where \( G^{B2} = G^{B19'+} \). The B2→R transformation at \( T^{B2-R} \), as indicated in the figure is thermodynamically prohibited. For heating from the martensite state, the system free energy state is expressed by \( G^{B19'-} \), and the reverse B19’→B2 transformation occurs at \( T^{B19'-B2} \) where \( G^{B19'-} = G^{B2} \).

Figure 2.6 (b) illustrates the phenomenon of transformation sequence of B2→R→B19’ on cooling and B19’→B2 on heating, as observed in Figure 2.5 (b). The shift of R-phase free energy lines to a lower position allows B2→R to occur when the system is cooled down to \( T^{B2-R} \) where \( G^{B2} = G^{R+} \). As the cooling continues, the R-phase remains as the stable phase of the system until the free energy of \( G^{R+} \) is equal to \( G^{B19'+} \). The occurrence of R-phase has delayed the martensite transformation to a much lower temperature of \( T^{R-B19'} \). The transformation on the reverse proceeds only in a single-step of B19’→B2 since the position of \( G^{R-} \) line is always above either \( G^{B19'-} \) or \( G^{B2} \).

Figure 2.6 (c) demonstrates how the R-phase transformation can also occur on the reverse transformation, making the transformation cycle a symmetrical B2↔R↔B19’, as seen in Figure 2.5 (c). When the R-phase free energy lines are shifted further down, it is possible for the R-phase free energy to be lower than those of the other two phases on both cooling and heating. The R↔B19’ transformation has a broader hysteresis than does the B2↔B19’, as been evident in (c).
2.2.2 Deformation Behaviour of NiTi

Near equiatomic Ni-Ti alloys experience peculiar deformation behaviour, as shown in Figure 2.7. The deformation is characterised by a stress plateau associated with the stress-induced martensitic transformation. Over the stress plateau, the deformation proceeds in a localised manner. This behaviour is referred to as the Lüders-type deformation [130-132]. During Lüders-type deformation, as schematically illustrated in (a), the alloy exhibits inhomogeneous strains along its length, with two distinct regions. Region “A” is untransformed austenite and its strain corresponds to $\varepsilon_A$. Region “B” is
the stress-induced martensite and its strain corresponds to $\varepsilon_B$. During the propagation of the stress plateau the strains inside the two regions remain unchanged but only the relative length fraction of region “B” expands at the expense of region “A”. Therefore, the local strain across the transformation interface between the two regions equals exactly the difference between $\varepsilon_A$ and $\varepsilon_B$, i.e. the length of the stress plateau. This localised manner of deformation may also proceed in multiple bands from which the stress-induced martensite nucleates from multiple locations, as shown in figure (b). Of this phenomenon, the deformation bands growth speed decrease as the number of bands increases [130, 131].

![Stress-strain curve with Lüders-type deformation behaviour of near-equatomic NiTi](image)

Lüders-type deformation observed in NiTi shape memory alloy represents the mechanical instability of its deformation behaviour. This has multiple adverse effects. It causes strain marks in tube drawing and similar NiTi production processes. It jeopardises strain controllability in load control situations in application. The localised strains also cause inhomogeneous fatigue of the component in service.

### 2.2.3 Deformation-Induced Martensite Stabilisation

It has been generally considered that $T>A_f$ being the criterion for shape recovery and pseudoelasticity. However, some recent studies have shown that deformed martensite, formed by either stress-induced martensitic transformation or martensite reorientation,
reverts back to austenite at increased temperatures [135-138]. Figure 2.8 illustrates this phenomenon where the reverse transformation of a deformed martensite on the first heating occurs at ~20 K higher than the undeformed sample of a near-equiaatomic NiTi alloy [138]. This phenomenon is known as “deformation induced martensite stabilisation.” A same effect can also be observed in another phenomenon as the increase of the stress hysteresis in pseudoelasticity resulting from the decrease of the reverse transformation stress [32]. This effect has been observed in a few shape memory alloys, including NiTi [138], NiTiNb [137], TiNiCu [51], CuAlNi [139] and CuZnAlMn [140], for both single crystal and polycrystalline materials [137, 141].

The magnitude of temperature increase of this stabilisation effect is influenced by several factors, mainly the deformation mode [42] and the level of deformation [142]. The deformation modes that may induce this effect have been reported to include tension [46], compression [139] and shear [142] via stress-induced martensitic transformation or martensite reorientation, and cold rolling [41, 135]. Lin et al. [135] reported that deformation via cold rolling of NiTi alloy increased the reverse transformation temperature by 120 K after a severe deformation of 40% thickness reduction, whereas more gentle deformation of NiTi via the martensitic transformation generally increases the reverse transformation temperature by up to ~30 K [42]. Tan and Liu [42] showed that the effects are similar from both stress-induced martensitic

![Figure 2.8. Martensite stabilisation as manifested by the increase of reverse transformation temperature [138]](image)
transformation and martensite reorientation. This implies that the final products of martensite from both deformation modes are microstructurally similar. Additionally, deformation to beyond the stress plateau in pseudoelasticity also causes a substantial decrease in the critical stress for the reverse transformation [32, 143], thus increases the stress hysteresis, implying the stabilisation of the deformed martensite.

Various hypotheses have been proposed to explain the mechanism of this deformation-induced stabilisation effect. Lin et al. [135] suggested that the structural defects, such as dislocations and vacancies produced during the deformation, caused the stabilisation by imposing a frictional resistance to the reverse transformation. Picornell et al. [139] attributed the phenomenon to the loss of twin boundary energy, which is a driving force for the reverse transformation, in the detwinned martensite. Piao et al. [137] suggested that the release of the elastic strain energy stored in the multi-variant martensite caused by deformation is responsible for the effect. As an extended view of this mechanism, Liu and Favier [142] proposed that the deformation not only relaxes the existing internal elastic energy that is stored in thermal martensite, but also creates opposite internal elastic stresses in the reoriented martensite that oppose its reverse transformation. In line with these observations, it is understood that the reverse transformation of the reoriented martensite involves thermal transformation and a mechanical work in overcoming the grain boundary resistance.

Such shift of the temperature for the reverse transformation has direct implications to the application of shape memory alloys. Applications that utilise the shape memory effect of the alloys involve self-motivated shape recovery of the alloys associated with the reverse transformation. Similarly, the pseudoelasticity effect is utilised either via thermally-induced or mechanical stress. An increase of the reverse transformation temperature (or a decrease of the reverse transformation stress in the case of pseudoelasticity) implies a retardation, or complete avoidance, of the shape recovery, thus failure of the function. Therefore, it is critically important to characterise and to understand the deformation-induced martensite stabilisation effect and its contributing factors. As mentioned earlier, the stabilisation effect is greatly influenced by alloy condition, especially the microstructure imperfection. In most cases, shape memory effect and pseudoelasticity behaviours are utilised from alloys that have undergone thermomechanical treatment for optimum effect. The treatments include partial annealing after cold working and ageing precipitation. Since these treatments modify
the microstructure of the alloys, the martensite stabilisation effect is also expected to be influenced by this change. However, the stabilisation effect in relation to partial annealing influence has never been reported, while it is known that the transformation stress, temperature and hysteresis are directly dependent on annealing temperature.

2.2.4 Effect of Alloy Composition

Owing to the structural requirement of the B2 ordering, properties of near-equiatomic NiTi alloys are very sensitive to composition variations from the equiatomic stoichiometry. Referring to the Ti-Ni binary phase diagram shown in Figure 2.1, it is easy to understand that Ni content has the most profound influence on these alloys. If a Ni-rich solid solution is quenched from above 1000°C, precipitation will be avoided and excessive Ni may be retained. This mechanism is impossible on the Ti-rich side. Of this nature, the effect of composition change on the transformation temperature is only observed at the Ni-rich side, while on the Ti-rich side, the transformation temperatures remain the same as for the Ti-50.0at%Ni. Figure 2.9 shows the composition-dependence of transformation temperature based on historical data published in the literature [144].

It is seen that the $M_s$ temperature decreases rapidly with increasing Ni-content at above 50.0at%, whereas at below 50.0at%Ni the $M_s$ temperature remains constant. On one hand, this phenomenon can be used as an effective way to tailor the transformation temperature for required applications, but on the other hand, this imposes a challenge in producing a desired alloy with precise composition control.

Transformation behaviour of NiTi alloy can also be modified by the addition of a third element. Fe addition is found to be effective in promoting the R-phase transformation and suppressing the B19’ phase transformation [145]. This is of particular interest when the application requires minimum displacement but high cycle stability. Meanwhile, the addition of Cu is effective to reduce the thermal hysteresis of the $A\leftrightarrow M$ transformation, e.g., from ~30 K to ~10 K for a Ti$_{50}$Ni$_{40}$Cu$_{10}$ [126]. In contrast, the $A\leftrightarrow M$ thermal hysteresis can be enlarged to ~100 K by the addition of 9at% of Nb [127]. Generally, the shape memory behaviour of Ni-Ti binary alloys cannot be used at temperature above 373 K due to the martensite transformation temperatures limitation. However, this disadvantage can be overcome by the addition of Pd or Pt [30, 128], where it is found that the addition of 30at% of Pd for Ni raised the $M_s$ transformation temperatures by 250 K [30].
2.3 Thermomechanical Treatment of NiTi

As discussed earlier, owing to the unique thermodynamic characteristics of thermoelastic martensitic transformations, properties of NiTi shape memory alloys are strongly affected by the metallurgical conditions and the matrix composition of the alloys. Therefore, various thermal and mechanical treatments have been used as effective tools to manipulate the behaviour of the alloys. With regard to the ability to produce precipitates, binary Ni-Ti shape memory alloys are divided into two subclasses: the near-equiatomic NiTi (<50.4at%Ni) and the Ni-rich type (>50.5at%Ni). Corresponding to these two types of NiTi alloys, there are two distinctive heat treatments used: anneal and ageing, respectively.

2.3.1 Cold Working and Annealing

This thermomechanical treatment is applied mainly to near-equiatomic NiTi. Cold work introduces high densities of dislocations and structural defects in the matrix. These defects generate internal stresses, strengthen the matrix and affect the martensitic transformations. Partial anneal at below the recrystallisation temperature alters
dislocation and defect structures to different levels, thus has the ability to tailor the transformation and mechanical behaviour to suit the need.

2.3.1.1 Cold Work and Hot Work

It is found that cold working drastically decreases the temperatures of both the forward and reverse transformations, particularly \( M_f / M_s \), and introduces the R-phase transformation, as shown in Figure 2.10 (a). In addition, the latent heats of the transformations are also reduced [136]. Hot working process is also normally carried out to form the alloy into intended shapes. The transformation temperatures of hot rolled NiTi are also reduced with increasing degree of rolling, as seen in Figure 2.10 (b). However, the decrease in transformation temperatures diminishes with increasing hot rolling temperature [146]. This effect is easily understood from the fact that hot working the alloy, particularly above 600°C allows partial recovery process and possibly recrystallisation to happen, which in turn minimises its effect on the martensite transformations. Therefore, this process is not regarded as a critical measurement in altering the overall behaviour of martensitic transformation.

Fig 2.10. Effect of work-hardening on transformation temperature; (a) cold-working [136] and (b) hot-working [146]
2.3.1.2 Effect of Anneal on Transformation Behaviour

Annealing after cold working negates the effect of cold work, through recovery and recrystallisation [35, 97, 99, 147]. This effect can be observed from thermal transformation behaviours, as shown in Figure 2.11 where the transformation temperatures gradually change with respect to annealing temperature for near-equiatomic NiTi [35]. It is seen that the $M_s$ and $M_f$ temperatures increased rapidly with increasing annealing temperature in the lower range corresponding to the dislocation rearrangement and recovery of the matrix. R-phase transformation is also induced in this lower range annealing temperature signifying the presence of internal mechanical resistance for the transformation. Annealing at above 850 K appears to cause no further change in both forward and reverse transformation temperatures and the $A\leftrightarrow R$ transformation ceases to occur. From these measurements, the recrystallisation temperature for this near-equiatomic alloy system may be estimated to be around 850 K, as indicated with vertical dashed in the figure.

![Figure 2.11](image_url)

Fig 2.11. Effect of annealing temperature on transformation temperature of near-equiatomic NiTi [35]

Additionally, partial anneal of cold-worked sample also causes an increase in transformation temperature interval as the annealing temperature decreases [17, 35, 135]. This effect implies the inhomogeneity of the transformation as a result of the microstructure imperfection and defect generated by the cold work deformation. The physical evidence to further confirm the direct relation between the microstructure
condition and the transformation behaviour is shown in Figure 2.12 [30]. As the homogeneous microstructure is achieved upon recrystallisation at 873 K, the transformation behaviour of this alloy remain unchanged, as seen in Figure 2.11 for annealing at above 850 K.

Fig 2.12. TEM micrographs of Ti-49.8at%Ni, show the evolution of recovery and recrystallisation of a cold-rolled and then annealed for 1 hr at; (a) as cold-rolled, (b) 673 K, (b) 773 K and (d) 873 K [30].

2.3.1.3 Effect of Anneal on Mechanical Behaviour

Partial anneal of cold-worked alloy also affects the deformation behaviour of NiTi. This can be seen in Figure 2.13 where the solution-treated and fully recrystallised samples shown in (a) exhibit no pseudoelasticity even at 14 K above the \( A_f \). Instead, these samples show a gradual increase of permanent plastic strain as the deformation temperature is increased, as illustrated by dashed lines below the horizontal axis. Figure
2.13 (b) illustrates how the partial anneal of cold-worked sample improved the shape recovery and pseudoelasticity of the alloy. Complete pseudoelasticity is always achieved at deformation temperatures above $A_f$ and good pseudoelasticity is still achievable even at 50 K above the $A_f$. This implies the increase of yield strength of the alloy as the main criterion for good pseudoelasticity [17].

Figure 2.13. Effect of thermomechanical treatment on tensile deformation for Ti-49.8at%Ni [107]: (a) As solution treated and (b) Annealed at 673 K for 1 hour after cold-working

Figure 2.14 summarises the effect of anneal temperature on the yield strength and critical stress for inducing the transformation in a Ti-50.2at%Ni alloy [17]. It is seen that the yield strength ($\sigma^{\text{AY}}$) increases rapidly with decreasing annealing temperature in the range below the recrystallisation temperature. The critical stress for stress-induced martensitic transformation ($\sigma^{\text{SIM}}$) is also expected to increase as the annealing temperature decreases within this lower temperature range. However, this data is not available for comparison for this similar alloy and testing conditions. Annealing at above the recrystallisation temperature caused the yield strength, stresses for stress-induced transformation and for martensite reorientation to increase moderately. It is easy to understand that the increase of yield strength with decreasing annealing temperature at below the recrystallisation temperature is due to the effect of strain hardening by the cold working. However, the increases of these stresses with annealing
temperature at above the recrystallisation temperature are not expected or explained in literature.

![Figure 2.14](image)

**Figure 2.14.** Effect of annealing temperature on yield strength and critical stress for transformation of Ti-50.2at%Ni [17]

The quantitative effect of annealing temperature towards transformation temperatures provides a very significant benchmark to understand and predict the deformation behaviours of the alloys at any application temperature and also to design an optimum annealing temperature range for any required application temperature and stress. However, the mapping of the effects of anneal has been achieved in the literature mostly from a “sufficiently high” level of cold-work percentage prior to anneal. This is because it is generally perceived that the amount of cold work has much less impact in influencing the transformation behaviour as compared to anneal temperature. This has caused many to overlook the effect of level of cold-work. However, as shown in Figure 2.11 and Figure 2.14, the behaviour of near-equiaxial NiTi alloys are most sensitively influenced by anneal within the range of recovery, and that the rate of recovery during anneal is expected to be directly influenced by the level of prior cold work [97]. In this regard, the severity of cold work in destroying the microstructure is expected to directly influence the recovery index of the alloy during the partial annealing process. This, however, has largely been neglected in the literature. Due to lack of this knowledge, inconsistent results are obtained and reported in the literature of the properties of NiTi after anneal. Realising the fact that the amount of cold work done in forming the
intended shape and dimension of the final component may vary depending on the initial size of the alloy and the machine limitation, it is important to quantify the actual change of transformation behaviour with respect to the amount of cold work prior to anneal. Other than ensuring the accurate determination of shape memory behaviours, this will also optimise the feasibility and cost of the thermomechanical treatment processes.

2.3.2 Ageing

Ageing is applied mostly to nickel-rich alloys of >50.5at%Ni for improving the pseudoelasticity. Ageing treatment of NiTi alloys is a complex issue. The effects are affected by several parameters including alloy composition, ageing temperature and ageing time, as well as the solution treatment conditions of the alloys. Due to this level of complexity, a complete knowledge of the effect of aging has not been established, although adequate empirical knowledge has been achieved to enable industrial production of NiTi alloys of required properties [108, 148-150].

Ageing treatment is normally done within the temperature range of 450-750 K [148, 151]. The time required in promoting the nucleation and growth of the precipitates is highly dependent on the initial alloy composition and the ageing temperature. Since the temperature range for ageing is typically similar with the temperature range for partial annealing, the shape memory behaviours of Ni-rich alloy are also possible to be modified by combined effects from both ageing and annealing. It has been reported that this combination is useful in increasing the stress level for pseudoelasticity [30]. On the other hand, this combined treatment is not practical for alloys with less than 50.5at%Ni since it requires unreasonable long time to promote precipitation, and therefore economically not feasible. Nevertheless, ageing treatment remains as the most profound and effective technique for Ni-rich alloys since it can be applied to any components geometry and the shape memory characteristics can easily be adjusted by controlling the temperature and time of the treatment.

As discussed in section 2.1.2, ageing induces a number of Ni-rich precipitates. Among them Ti$_3$Ni$_4$ is the most influential to the properties of the alloys. Ti$_3$Ni$_4$ is a coherent precipitate [106, 113, 114]. It influences the transformation behaviour of NiTi via the stress fields it creates and the change to the matrix composition [30]. In contrast, Ti$_2$Ni$_3$ and TiNi$_3$ are incoherent and exist only as secondary phase inclusions in the matrix.
Their only effect on transformation behaviour may be due to the variation of Ni content in the matrix associated with their formation and dissolution [30, 102]. Over growth of Ti$_3$Ni$_4$ will lead to its conversion to Ti$_2$Ni$_3$ and TiNi$_3$, losing its influence on the transformation and mechanical behaviour of the alloy.

Ti$_3$Ni$_4$ may precipitate preferentially along grain boundaries during the early stages of ageing [110, 152], causing long-range microstructural inhomogeneity in the matrix, as seen in Figure 2.15 (a) for Ti-50.6at%Ni. A more uniform precipitate distribution will be formed if the alloy is aged at longer time. Similarly, a uniform distribution is achieved for alloy with higher Ni composition. This could happen because the nucleation driving force in the grain interior is relatively as high as the driving force near grain boundary [151]. This allows the precipitate to nucleate anywhere in the matrix, as seen in Figure 2.15 (b) for Ti-51.5at%Ni. Although the nucleation of precipitate for alloy with higher Ni solution concentration produces a uniform precipitate distribution, the initial nucleation is still near grain boundary, but this incident is hard to capture if the ageing temperature is high.

![Figure 2.15. TEM micrographs showing the precipitates distribution after ageing at 723 K for 1 hour in: (a) Ti-50.6at%Ni and (b) Ti-51.5at%Ni [151]](image)

### 2.3.2.1 Effect of Ageing on Transformation Behaviour

The response of NiTi alloy transformation behaviour to ageing treatment is also complex. Ageing introduces the R-phase transformation [129, 153]. Figure 2.16 shows the two exemplary transformation behaviours induced by ageing in comparison with the original transformation behaviour of a Ti-50.9at%Ni alloy. Sample (b) exhibits a transformations sequence of B2→R→B19’ on cooling, which all occur at higher temperatures than the single step B2→B19’ transformation in the solution treated sample (curve (a)). As the sample is aged at different condition, as shown in (c), the
transformations evolve into two-step transformations sequence of $B2 \leftrightarrow R \leftrightarrow B19'$, both on cooling and heating, with further suppression of $R \rightarrow B19'$ transformation to a much lower temperature. It has been reported also that ageing at temperatures below 600 K for short time caused suppression of the original $B2 \rightarrow B19'$ transformation without the occurrence of the R-phase transformation [121]. Since precipitate is less likely to be present at this stage, this effect is attributed to atomic rearrangement in the fashion of GP zones in the matrix as a precursor phenomenon for precipitation. On the other hand, it is also observed that ageing at higher temperature to above 723 K for alloy with $>50.8\text{at\%Ni}$ for long time may increase the $M_s$ and $M_f$ temperatures and the absence of R-phase [154]. This phenomenon is largely due to the depletion of Ni in the matrix as a result of the formation of large in size and high in volume of the incoherent precipitates.

Figure 2.16. Effect of ageing on transformation behaviour of Ti-50.9at\%Ni [129]

Ageing is also found to cause “multi-stage” transformation behaviour [108, 119, 121, 129, 149-151, 155]. Figure 2.17 shows DSC measurements of such multi-stage transformations behaviour observed in aged Ti-50.9at\%Ni alloy [129]. In (a) the alloy exhibited two separate stages of $R \rightarrow B19'$ transformation. In (b) the sample experienced a two-stage $B2 \rightarrow R$ transformation. In both cases, the reverse transformation may also exhibit either two-stage $B19' \rightarrow B2$ or $B19' \rightarrow R$ transformations. This phenomenon is
generally observed in ageing at lower temperature and shorter time, and easily captured in lower Ni-rich matrix of less than ~51at%Ni [129, 150, 156].

![Figure 2.17. Multistage transformation behaviours variants observed in Ti-50.9at%Ni: (a) two separate stages of R-M transformation and (b) two-stage A-R transformation [129]](image)

Different mechanisms have been proposed for these multistage transformation behaviours. Bataillard et al. [157] proposed the mechanism based on stress relaxation, in relation to “stressed” and “unstressed” regions at the microscopic scale near precipitates. Khalil-Allafi et al. [110] proposed a mechanism based on long-range heterogeneous distribution of Ti$_3$Ni$_4$ along grain boundaries and in the interior of grains, evidenced by detailed TEM observations, effectively dividing the matrix into two different alloy conditions. This observation leads to a more logical and convincing explanation for the multi-stage transformations, which was later adopted and extended by others [121, 149-151, 158]. Zheng et al. [121] later further extended the theory by combining the effects of long-range heterogeneity of precipitate structure between grain boundaries and grain interior and short-range heterogeneity caused by over-growth of coherent precipitates into the formation of incoherent precipitates, as shown in Figure 2.18. In this theory, the ageing process is divided into five stages, corresponding to I - suppression of the original B2$\rightarrow$B19'; II – appearance of B2$\rightarrow$R; III - transformation sequence of B2$\leftrightarrow$R$\leftrightarrow$B19'; IV – multistage transformation of B2$\leftrightarrow$R$\leftrightarrow$B19’ and B2$\rightarrow$B19'; and V – restoration of B2$\rightarrow$B19’ at higher temperatures. This theory appears
to be the most credible to date, being able to rationalise each transformation sequences in relation to the precipitate distribution and coherency with the matrix.

Figure 2.18. Schematic illustration to describe the evolution of precipitation growth in relation to multistage transformations observed in aged Ni-Ti alloys [121]

2.3.2.2 Effect of Ageing on Mechanical Behaviour

Largely owing to the effect of precipitation hardening, ageing is effective in influencing the mechanical behaviour of NiTi by raising its yield strength. The increase of yield strength allows the alloy to be deformed via stress-induced transformation within a wider temperature window above $A_f$ without slip, thus enabling reversibility (i.e. pseudoelasticity). This hardening effect is highly dependent on the control of ageing temperature, time and alloy composition. Figures 2.19 and 2.20 illustrate this phenomenon for a Ti-50.6at%Ni alloy, where the samples aged at 673 K exhibit much superior pseudoelasticity and shape memory effect as compared to the samples aged at 773 K [30]. Figure 2.21 shows the effect of ageing temperature on the critical stresses of pseudoelasticity. It is seen that the sample aged at the lowest temperature has the highest stress for the forward transformation but exhibits poor pseudoelasticity. Such observations demonstrate that ageing of NiTi is a complex matter dictated by three independent parameters. To date, a comprehensive database of the effects of ageing on the mechanical properties of NiTi has not been established in the literature, although major commercial manufacturers often have adequate in-house empirical knowledge to guide for the production of high quality pseudoelastic NiTi.
Figure 2.19. Tensile deformation behaviour of Ti-50.6at%Ni aged at 773 K for 1 hr [30].
Figure 2.20. Tensile deformation behaviour of Ti-50.6at%Ni aged at 673 K for 1 hr [30]

Figure 2.21. Effect of ageing on forward and reverse stress-induced transformations behaviour of Ti-50.6at%Ni [107]
2.3.3 Oxidation

Generally, heat treatment induced oxidation has not been a major concern in production and processing of NiTi alloys, largely due to their high intrinsic oxidation resistance. However, limited experimental findings reported in the literature indicate that NiTi alloys experience certain degree of oxidation and oxidation affects the transformation and mechanical behaviour of the alloys [151]. Excessive oxidation is expected to impair the shape memory properties, by two reasons. (1) The oxide, being brittle ceramic phase, shows no martensitic transformation and no shape memory effect, thus functions as a pure mechanical resistance to shape memory deformation and recovery. (2) Due to the difference in affinity to oxygen, Ti oxidises more preferentially than Ni, causing Ni-enrichment to the matrix composition.

In fact, the latter has been exploited in medical application of NiTi, in which a thin surface layer of rutile (TiO$_2$) is encouraged to form by in-situ conversion in oxidising environment as a shield to prevent Ni release into the bio-system [159]. In these studies, the concern of surface oxidation has been focused on the biocompatibility of the alloys and its effect on shape memory properties has largely been overlooked. One reason for this neglect could be due to the fact that the oxide layer formed is usually very smooth and thin, especially when the alloy is heat treated at below 500°C [160]. However, with regard to NiTi thin film materials and miniaturisation of shape memory devices, the thin oxide layer could be critical in affecting the properties of the materials and the performances of the devices. Therefore, the oxidation issue requires a critical quantification. Also, if the treatment temperature is elevated to above 600°C, the oxide layer formed is not only rough and thick but may also porous structure and multi-layers of different phases underneath the rutile. These layers have been identified as the mixture of TiNi$_3$, TiNiO$_3$, Ni(Ti), and Ti$_3$Ni$_4$ phases [103, 160-163]. Figure 2.22 shows an example of the different phases formed from the oxidation process occurred in Ti-50at%Ni.
The presence of these multi-phases beneath the rutile is expected to affect the transformation behaviour of the alloy. Nishida et al. [164, 165] relate the oxidation to the occurrence of R-phase transformation and two-step of martensite transformations. Although these multi-stage transformations are related to the presence of Ti$_3$Ni$_4$ precipitate from the heat treatment, they claimed that the heterogeneity of precipitate particles in the matrix can be suppressed if oxidation can be avoided, thus prohibits the two-step martensite transformation, as can be seen in Figure 2.23. On the other hand, Zhang et al. [103] demonstrated that titanium is very reactive with oxygen at high temperatures. Thermodynamically, to avoid the oxidation reaction of TiNi + O$_2$ $\rightarrow$ TiO$_2$ + Ni at 1000°C requires below 10$^{-26}$ atm of oxygen partial pressure.

This matter has been overlooked by Honma et al. [166] in conducting their experiment in proposing the order-disorder behaviour in this alloy. It has been shown [103, 167] that selective leaching of titanium to form oxide on the surface causes the region underneath to be enriched with nickel, eventually leading to the eutectic melting of 57at%Ni and 75at%Ni at 1118°C, as seen in the Ti-Ni binary phase diagram [101]. This behaviour has been mistakenly identified as the “order-disorder” behaviour by Honma et al. [166].
Figure 2.23. DSC cooling curves of Ti-50.6at%Ni aged at 773 K for various periods in two different environments: (a) oxidising and (b) non-oxidising [164]
3.1 Research Objectives

The main interest of this study is to investigate the processing of engineering NiTi alloys for optimum shape memory properties. The study has two main experimental objectives:

(1) To quantify the effects of thermomechanical treatments on NiTi alloys and, based on the knowledge, to characterise their optimum shape memory properties resulting from these treatments; and

(2) To create novel structured NiTi by means of thermomechanical treatments.

With respect to objective (1), the specific tasks include:

(1) Effect of the level of cold work on the response of the alloys towards anneal

(2) Anneal temperature dependence of the effect of deformation-induced martensite stabilisation

(3) Surface oxidation and Ti-depletion caused by high temperature heat treatment

With respect to objective (2), the specific tasks include:

(4) Creation of functionally graded NiTi by heat treatments
3.2 Experimental Design

3.2.1 Effect of Cold Work

The purpose of this experiment is to quantify the effect of the amount of cold work on the response of NiTi towards anneal treatment. This corresponds to the known fact the shape memory behaviour of NiTi is very sensitive to microstructural defects and imperfections [17, 35, 135]. The general practice in both research and in industrial production is to cold work NiTi alloys to sufficiently large area-reductions or length-elongations for anneal, with the general assumption that the amount of cold work does not contribute significantly to the end result of anneal and the final microstructure and properties of NiTi alloys are only determined by the time and temperature of the anneal. However, given that recovery process is dependent on the severity of cold work as well as the time and temperature of the annealing, the effect of severity of cold work should also be investigated. To date there are very limited systematic investigation of this aspect reported in the literature [97, 99]. Such knowledge is of direct relevance to industrial production of NiTi as well as to interpretation of research experimental results.

3.2.2 Effect of annealing temperature on martensite stabilisation

This experiment aims to quantify the anneal temperature-dependence of the martensite stabilisation effect of NiTi. The knowledge of the extent of martensite stabilisation effect is essential for design when using these alloys. As discussed in Chapter 2, martensite stabilisation is recognised as the increase of the transformation hysteresis in either temperature or stress via the increase of the reverse transformation temperature or the decrease of the reverse transformation stress. This phenomenon is observed to be effectively produced by deformation and is highly dependent on the amount of deformation. This implies the influence of microstructure imperfections of the alloy and therefore is also expected to be influenced by the history of its thermomechanical treatment. However, this has never been analysed, and in most cases the stabilisation is observed from fully recrystallised samples. In many applications NiTi are used in partially annealed states. The uncertainty of the effects of partial annealing on the stabilisation effect leads to incorrect estimation of the critical conditions for applications of these alloys.
3.2.3 Oxidation and Ti-Depletion

The objective of this experiment is to determine the extent of surface oxidation and Ti-depletion caused by high temperature heating both in air and in inert gas environments, and their effects on the shape memory and transformation behaviour of NiTi. High temperature heat treatment is inevitable for NiTi alloy production and processing. Although the alloying process is carried out in vacuum, the subsequent treatments such as hot-working, annealing and ageing are normally conducted in air. It is known that titanium is very reactive and therefore a prolonged exposure to air at elevated temperatures, e.g. in ageing treatment, poses the risk of preferential leaching of titanium from the surfaces of the alloy due to oxygen. In addition, the surface oxide layer is effectively a ceramic coating, incapable of martensitic transformation and shape memory effect. Such changes are expected to affect both the transformation behaviour and the mechanical properties, thus shape memory behaviour of the alloy, given that properties of near-equiatomic NiTi alloys are very sensitive to alloy composition changes. To address this issue, this experiment analyses the oxidation of NiTi when heated to various temperatures for different times, in air and in argon. The severity of oxidation is measured from the thickness of the oxide as observed by means of SEM.

3.2.4 Functionally graded NiTi

The objective of this experiment is to create functionally graded NiTi material with continuously varying thermomechanical properties, for example along the length of a NiTi wire, achieved by modifying the microstructure of the alloy. As discussed in Chapter 2, the transformation temperature interval in NiTi is small, typically <10 K. The stress interval of a stress-induced transformation is intrinsically related to the thermal interval, and is small, too. When deforming in tension in Lüders deformation mode, the stress window for the transformation is effectively zero, rendering the material total uncontrollable by stress. To improve this limitation, it is necessary to expand the transformation intervals.

A possible approach to expanding transformation interval is to create functionally graded NiTi in which the martensitic transformation may occur at a different temperature (or stress) at one end than at the other. This may be achieved by having either a gradient composition or a gradient microstructure for NiTi. The approach of gradient microstructure is feasible in relation that the microstructure of near-equiatomic
Ni-Ti is very sensitive to annealing temperature after cold work, which in turn alters its transformation temperature and transformation stress. Realising this potential, it is feasible to design a way that a piece of material undergoes a gradient temperature annealing. This would allow the material to respond to the external stimuli for transformation in a gradient manner, providing improved transformation controllability. In addition to annealing, this microstructure modification is also feasible for differential ageing with either gradient temperature or gradient time.

In this experiment, the property gradient, or the microstructural gradient of the matrix, is to be created by gradient temperature heat treatment, both gradient anneal after cold work for near-equiatomic NiTi alloys and gradient ageing after solution treatment for Ni-rich alloys. The most suitable temperature profile for the temperature gradient is selected from 500 K to 800 K. The continuous gradient of the microstructure is verified from the thermal transformation behaviour measured from samples taken along the length of the wire. Meanwhile the gradient stress for transformation is observed from tensile deformation behaviour. The outcome of such gradient materials provides a new potential in improving controllability for shape memory actuation and sensing applications.

3.3 Experimental Procedure

3.3.1 Materials Selection

The heat treatments processes carried out in this scope of study involved mainly annealing and ageing. As mentioned in the previous section, Ni-rich alloys are very responsive to precipitation at elevated temperature and complicate the transformation sequence and behaviour. In most of the cases of this work, the treatment temperatures fall between 550 K and 800 K. This temperature range works for both annealing and ageing. Therefore, to avoid complication caused by precipitate formation, only alloys with 50.0-50.5at%Ni were used in all experimental work except for the ageing treatment. For the experimental work on the effect of ageing, a Ti-50.8at%Ni alloy was used. All materials used were obtained from commercial suppliers in the form of wires with different diameters ranging from 0.5 to 3 mm in diameter.
3.3.2 Effect of Cold Work

The alloy used for this experiment is Ti-50.5at%Ni wire of 1.4 mm in diameter. The wire was initially solution treated at 1123 K for 3.6 ks in argon. Then the wire was cold rolled at room temperature to different elongation percentages, including 15%, 35%, 67%, 95% and 170%. The 15% wire elongation was achieved by a single pass rolling whereas the other percentages were achieved by multiple-pass rolling. Following the cold working, the wires were annealed for 3.6 ks at different temperatures ranging from 573 K to 923 K. The thermal transformation behaviour and mechanical behaviour of the heat treated alloys were analysed by means of DSC and tensile testing, respectively.

3.3.3 Martensite Stabilization

The material used in this study was a commercial Ti-50.2at%Ni alloy in wire form with original diameter of 1.4 mm. The wire was cold-rolled at room temperature to 30% elongation by length. Then the wire was cut into 30 mm long sections and annealed at different temperatures ranging between 623 K and 923 K for a period of 3.6 ks. The specimens were cut using diamond cutter, which is considered to cause none or negligible plastic deformation at the cutting ends, thus does not affect transformation behaviour. In addition, the end sections of the cut samples were polished to remove any possible volume of the sample that may have been deformed to any extent. This matter has been taken into careful consideration during sample preparation. After annealing the samples were quenched into cold water and the surface was lightly cleaned mechanically using fine abrasive papers to remove oxide. Thermal transformation behaviour for the as-annealed samples was initially determined prior to tensile deformation be used for comparison. Tensile deformation was conducted at two different temperatures. The first set was conducted in air at the ambient temperature of 293 K and the second set was conducted at 313 K using a liquid bath. The wire was unloaded upon reaching the end of the stress-plateau of the Luder’s-type deformation behaviour. Thermal transformation behaviour of the wires after the deformation was analysed by means of DSC. The samples for DSC measurement were cut from within the gauge length of the tensile samples. For each DSC measurement, the sample was first cooled in liquid nitrogen to ensure a complete martensitic state.
3.3.4 Oxidation and Ti-Depletion

The material used for this study was Ti-50.5at%Ni wire with the diameter of 1.50 mm. The wire was cut into three sets for different analyses. The samples of the first set were for DSC measurements and were cut into an average mass of 20 mg. The second set was for tensile deformation and were cut into 40 mm in length. The last set was for SEM and EDS analyses and was ~2 mm in length. All samples were then heat treated at different temperatures up to 1273 K and for different periods of time up to 24 hours. The heat treatment was conducted in two different environments of air and flowing argon, using a tube furnace.

Following the heat treatment, the DSC measurements were carried out for each of the conditions and the samples were used as they were, i.e., without removal of oxide layer from the surfaces. Similarly, tensile deformation was carried out on every sample in their as-heat treated state. For SEM and EDS analyses, samples were mounted in epoxy for easy handling and ground and polished on one end to expose the transverse surface of the interior as illustrated in Figure 3.1.

![Figure 3.1. Schematic illustration of EDS preparation for oxidised sample](image)

3.3.5 Gradient Temperature Annealing

In this experiment a temperature gradient is created in a tube furnace for annealing, as illustrated in Figure 3.2. The tube length of the furnace is 275 mm and the diameter of the hearth is 40 mm. By utilising the natural phenomenon of free convection, the
temperature gradient was achieved by leaving one end of the furnace tube open to the ambient whereas the other end was blocked with a refractory insulator. The temperature distribution along the hearth of the furnace was measured with 12 thermocouples set at 20 mm equal intervals along the length of the furnace tube. The furnace thermostat was positioned at an offset distance of 180 mm from the open end of the tube.

Figure 3.2. Schematic illustration of the tube furnace cross section

The temperature profiles along the hearth of the furnace at different setting temperatures are plotted in Figure 3.3. As seen in the figure, gradient temperature profiles are achievable for between 0 and 150 mm along the length of the hearth of the furnace, with temperature differences as large as 570 K when the setting temperature is 973 K. The linearity of temperature gradient improves as the setting temperature increases. Also, the range and magnitude of temperature gradient can be varied by choosing a specified setting temperature.
The materials used for this study were Ti-50.2at%Ni and Ti-50.5at%Ni in the form of wire with diameters of 1.5 mm and 1.2 mm, respectively. The wires were initially solution treated at 1123 K for 3.6 ks to eradicate any effect of prior treatments including cold working and ageing. The wires were then rolled at room temperature to 50% elongation in length. Two sets of samples were cut from the wires, short samples of 40 mm in length and long samples of 120 mm in length. The short samples were annealed at different set temperatures (referred to as isothermal samples). These sets of short samples were used to quantify the actual effects of annealing temperatures and subsequently to verify the gradient behaviour of the long samples. The long samples (referred to as gradient samples), were annealed in a gradient temperature in the tube furnace at the setting temperature of 823 K. This setting temperature produces a relatively good linear temperature profile from 550 K to 800 K. This setting temperature also provides a reasonable length of temperature gradient to use for the long wires. The 100 mm gauge length wires were inserted in the furnace with one end positioned at 600 K and the other end positioned at 800 K, as shown in Figure 3.4. The treatment was conducted in air for 3.6 ks.
3.3.6 Gradient Temperature Ageing

This treatment utilised the same tube furnace to age the alloy in a gradient temperature field. The alloy used was Ti-50.8at%Ni wire of 0.80 mm in diameter. The wire was initially solution treated at 1123 K for 3.6 ks in Argon to eliminate the effects of all prior treatments. Two sets of samples were made, short wires of 40 mm in length for isothermal ageing and long wires of 120 mm long for gradient temperature ageing. Isothermal ageing of the short wires was carried out at 573 K, 623 K, 673 K, 723 K and 773 K for different times ranging from 15 minutes to 24 hours. Gradient temperature treatment for the long wires was done by positioning samples with the gauge length at between 575 K and 800 K, as shown in figure 3.4, a similar temperature setting with the gradient anneal process. The treatment was conducted in air for 1 hour, 2 hours, 4 hours and 8 hours.

3.4 Material Properties Analysis

3.4.1 DSC Analysis

Transformation behaviour of the various samples was analysed by means of DSC using a TA Q10 differential scanning calorimeter instrument. All measurements were conducted in N$_2$ environment with a cooling/heating rate of 10 K/min. Specimens for
measurement were cut from wires by using a low speed diamond saw to avoid excessive deformation. Sample masses ranged from ~5 mg for thin wire samples to 20 mg for samples from thick wires. An indium reference sample was used for temperature and energy calibration.

### 3.4.2 Tensile Deformation

Tensile deformation was carried out using an Instron 4301 universal testing machine. The deformation was conducted in air or in water for elevated temperatures using a liquid bath. The liquid bath enabled temperature control at between 270–380 K with an accuracy of ±0.5 K. In most cases, the gauge lengths of the samples for tensile deformation were between 20 mm to 30 mm. The cross-head speed was 0.5 mm/min, corresponding to strain rates of 2.8-4.2x10⁻⁴/s. In some cases, the cross-head speed was set to 1 mm/min for samples with gauge lengths greater than 40 mm. These strain rates are low enough to ignore the thermal effect associated with the latent heat of the martensitic phase transformation.

### 3.4.3 Thermomechanical Measurement

Thermomechanical analysis was conducted using a Shimadzu thermal mechanical analyser (TMA). Samples for thermomechanical testing were cut by means of electrical discharge machining from the deformed billets into thin wires of 0.25x0.35x20 mm³, with a gauge length of 10 mm. Testing was conducted by varying temperature at a cooling/heating rate of 10K/min between 260 K to 420 K, whilst maintaining a constant stress within the range of 20–250 MPa.

### 3.4.4 Scanning Electron Microscopy and X-ray Energy Dispersive Spectrometry

Scanning electron microscopy (SEM) and X-ray energy dispersive spectrometry (EDS) analyses were carried out using a Zeiss 155 high resolution scanning electron microscope. SEM images were taken using secondary electron detector with 3–15 kV setting of electron beam. In some cases an in-lens is used to enable a short working distance of ~5 mm, which enables high imaging resolution of ~10 nm. Chemical analysis by EDS was carried out with the equipment conditions of 20 kV electron beam and 16 mm of working distance. This setting produces an electron beam size of about 10 nm which yields an estimated spatial resolution of ~1 μm for composition analysis.
CHAPTER 4

INFLUENCES OF COLD WORK LEVEL AND PARTIAL ANNEAL

This chapter presents the experimental evidences and discussions of the influence of partial annealing towards shape memory behaviour of NiTi alloys. This chapter is divided into two sections. The first section quantifies the influence of the level of cold working and partial annealing temperature on thermal transformation and tensile deformation behaviours. The second section quantifies the influence of partial annealing temperatures on martensite stabilisation effect. The experiments were carried out using near-equatomic NiTi wires.

4.1 Cold Work and Partial Anneal

In many practices of materials production and application, NiTi shape memory alloys are often cold worked and annealed for shaping or to achieve desired properties. The level of cold work needs to be sufficiently high to enable effective subsequent heat treatments, considering that the shape memory effect is able to produce \(~10\%\) recoverable strain. Whereas the necessity of having sufficient pre-cold work is fully recognised, the actual knowledge of the critical level and the effects of the level of cold work are scarce in the literature. On the other hand, it is also known that desirable shape memory and pseudoelastic properties are obtained with partial anneal at below the critical temperature for recrystallisation. In addition, for commercial production of shape memory alloys this thermomechanical treatment requires optimum settings in order to minimise the cost. Excessive cold working and heat treatment at high temperature imply higher production cost. Therefore, it is of both scientific interest and practical importance to understand the effects of cold work and the subsequent heat treatment on shape memory behaviour. The material used in this analysis was Ti-50.5at\%Ni wire with the initial diameter of 1.5 mm.
4.1.1 Effect of Annealing Temperature

4.1.1.1 Thermal Transformation Behaviour

Figure 4.1 demonstrates the evolution of thermal transformation behaviour of Ti-50.5at%Ni with respect to the variation of annealing temperature. The samples were previously cold rolled by 67% elongation and subsequently annealed at different temperatures for one hour. DSC samples were prepared by cutting small sections from the wire using diamond cut off wheels in order to minimise severe deformation at the cutting edges. The sample annealed at 873 K exhibited a single peak transformation of B2→B19’, representing a complete recrystallisation of the microstructure. The peak temperature for the forward transformation (B2→B19’) of this sample was measured to be $T_{A-M} = 280$ K and that for the reverse transformation (B19’→B2) was $T_{M-A} = 313$ K. When the deformed alloy was annealed at below the recrystallisation temperature, the transformation preceded by B2→R→B19’ on cooling and B19’→B2 on heating, as shown in the sample annealed at 823 K. Further lowering the annealing temperature to 723 K resulted in two-stage transformation behaviour of B2↔R↔B19’ and reduced the transformation latent heat.

Figure 4.2 summarises the change of thermal transformation temperatures with respect to annealing temperature, as extracted from Figure 4.1. The transformation temperatures used represent the peak temperatures of the transformations. The effect may be divided into two distinct regions in annealing temperature. Region I is above 850 K, where the alloy exhibited a single stage B2↔B19’ martensitic transformation and the transformation temperatures appeared to be independent of the anneal temperature. This temperature (850 K) is identified the recrystallisation temperature for this alloy. Region II is below 840 K. In this region the alloy was partial annealed (recovered, but not recrystallised). The transformation sequence in this region was B2→R→B19’on cooling and B19’→B2 on heating, which later evolved into B19’→R→B2 with lowering the annealing temperature. On cooling, $T_{R-M}$ decreased rapidly and $T_{l-R}$ increased steadily with decreasing annealing temperature, thus widening the apparent temperature interval of the transformations. Further decreasing the anneal temperature to below 660 K led to negligible change of transformation temperatures on both cooling and heating. However, the transformation peaks were further widened as the annealing temperature lowered, as previously seen in Figure 4.1.
Figure 4.1. Thermal transformation behaviour of Ti-50.5at%Ni after partial anneal at different temperatures for one hour.

Figure 4.3 shows the effect of annealing temperature on the transformation enthalpy change. On heating, $\Delta h^{M-A}$ represents the latent heat of B19'→B2 transformation and was measured from samples annealed at above 773 K. This latent heat decreased slowly as the annealing temperature decreased. Samples annealed at 723 K and below exhibited B19''→R→B2 transformations and the two transformation peaks overlapped, as seen in Figure 4.1. Therefore, the measured latent heat of $\Delta h^{M-R-A}$ represents the combined heats of B19'→R ($\Delta h^{M-R}$) and R→B2 ($\Delta h^{R-A}$). On cooling, $\Delta h^{A-M}$ represents the latent heat of single stage B2→B19' transformation measured from fully recrystallised samples. $\Delta h^{\text{Total Cooling}}$ represents the summation of latent heats measured separately from the A→R ($\Delta h^{A-R}$) and R→B19' ($\Delta h^{R-M}$) transformations. As the annealing temperature decreased, $\Delta h^{A-R}$ remained nearly unaffected but $\Delta h^{R-M}$ decreased severely. Comparing the total latent heats, it is seen that $\Delta h^{M-R-A}$ ($\Delta h^{M-A}$) is always higher than $\Delta h^{\text{Total Cooling}}$. 
Figure 4.2. Effect of annealing temperature on transformation peak temperatures of Ti-50.5at%Ni

Figure 4.3. Effect of annealing temperature on enthalpy changes of the transformations of Ti-50.5at%Ni
4.1.1.2 Tensile Deformation Behaviour

Figure 4.4 shows the deformation behaviour of the alloy after partial anneal at different temperatures. The deformation was carried out in tension at 313 K with the cross-head speed of 0.5 mm/min. Samples annealed at 873 K and 923 K are fully recrystallised. They show similar behaviour where the forward stress-induced martensite transformation occurred at about 170 MPa and the stress plateau extended to about 10%, with 9% transformation strain. The critical stress to induce the forward transformation ($\sigma_{\text{fwd}}$), steadily increased as the annealing temperature decreased to below 823 K. Samples annealed at below 773 K showed good pseudoelasticity at the testing temperature of 313 K. It is also noted that the Lüders type deformation behaviour (the stress plateaus for the forward and the reverse transformations) became less defined when anneal temperature decreased. The deformation behaviour gradually evolved into uniform deformation when annealing temperature was below 623 K. It is also apparent that the anneal temperature of 573 K was too low to induce adequate recovery in the matrix and therefore the deformation was in effect a mixed process of plasticity and martensitic transformation. The transformation strain continued to decrease as the annealing temperatures decreased.

![Figure 4.4](image_url)

Figure 4.4. Deformation behaviour of stress-induced martensitic transformation of Ti-50.5at%Ni samples annealed at different temperatures after cold work
Figure 4.5 summarises the results extracted from Figure 4.4, showing the effect of annealing temperature on the critical stresses and the transformation plateau strains for the forward and reverse stress-induced transformations. As seen in (a), both the forward ($\sigma^{fwd}$) and the reverse ($\sigma^{rev}$) stresses increased as the annealing temperature decreased. $\sigma^{rev}$ decreased more rapidly than $\sigma^{fwd}$, resulting in widening of the stress hysteresis ($\sigma^{hys}$) of pseudoelasticity with increasing annealing temperature. However, $\sigma^{hys}$ remained nearly constant at about 250 MPa for the samples annealed at above 673 K. The reverse transformation was not expected to occur on unloading for samples annealed at above 823 K, since the deformation temperature was below or too close to the $A_f$ temperature and also an addition of the effect of martensite stabilisation after the deformation, which shifted the $A_f$ to higher temperature.

Figure (b) shows the effect of anneal temperature on the forward ($\varepsilon^{fwd}$) and reverse ($\varepsilon^{rev}$) plateau strains. It is seen that both $\varepsilon^{fwd}$ and $\varepsilon^{rev}$ increased as the annealing temperature increased. It is also evident that $\varepsilon^{fwd} > \varepsilon^{rev}$. The maximum value of $\varepsilon^{fwd}$ was $\sim 9\%$ after annealing at 873 K. Samples annealed at above 773 K showed no pseudoelasticity at this testing temperature.

These results are consistent with previous studies [17, 35, 135]. The complete data shown in Figure 4.5 provide useful guide for the design of NiTi materials via heat treatment for controlled properties, in particular functionally graded NiTi by means of heat treatment in gradient temperature fields.
4.1.2 Effect of Cold Work Percentage on Thermal Transformation Behaviour

Figure 4.6 shows the DSC measurement of samples cold worked to different elongation percentages prior to annealing. The annealing was done at 723 K for one hour for all the samples. It is seen that there is a progressive evolution of the transformation behaviour with respect to the level of prior cold work, most noticeably the temperature of the R→B19' transformation on cooling decreased with increasing level of prior deformation. The B2→R transformation remained at about the same temperature regardless of the amount of cold work. Transformation on heating is also seen to split into two transformations of B19'→R and R→B2 with increasing cold work. The R→B2 transformation remained unchanged with respect to the level of the cold work.

![Diagram showing transformation behaviour](image)

Figure 4.6. Effect of prior cold work on the thermal transformation behaviour of Ti-50.5at%Ni annealed at 723 K

Similar behaviour has also been seen with samples annealed at other temperatures. Figures 4.7 and 4.8 show the transformation behaviour of samples annealed at 823 K and 623 K, respectively. The samples annealed at 823 K, which is close to the recrystallisation temperature (850 K), showed very little variation for different levels of prior cold work, as seen in Figure 4.7. Annealing at 623 K, as shown in Figure 4.8,
appears to have caused insufficient recovery and only weak transformations were observed, even for low levels of cold work.

![Graph showing thermal transformation behaviour of Ti-50.5at%Ni](image)

**Figure 4.7.** Effect of prior cold work on the thermal transformation behaviour of Ti-50.5at%Ni annealed at 823 K

Figure 4.9 shows the effects of cold work on transformation temperatures of the samples after annealing at different temperatures. The scales on both figures are made equal for direct comparison of the temperature change. Figure 4.9 (a) shows the peak temperatures of the B19'→R ($T_{M-R}^{M}$) and R→B2 ($T_{R-A}^{R}$) reverse transformations. Only samples annealed at below 723 K were shown because the transformation for all samples annealed at above 773 K exhibit only single peak of B19'→B2 and the temperature remained constant. Similarly, samples that were cold worked at 15% were not shown here because their transformation involved only single peak of B19'→B2. This implies that internal resistance created in the matrix from the 15% of cold work was thermodynamically insufficient to induce R-phase on the reverse transformation.

Figure 4.9 (b) shows the peak temperatures of the B2→R ($T_{A-R}^{A}$) and R→B19' ($T_{R-M}^{R}$) forward transformations on cooling. The B19'→B2 peak temperatures ($T_{M-A}^{M}$) for samples annealed at 873 K are included in (a) for direct comparison of their positions.
relative to those of $T_{M-R}$ and $T_{R-A}$. It is seen that $T_{M-A}$ remained constant at $\sim 312$ K for all levels of cold work. This implies that the recrystallisation temperature is independent of the level of cold work. Similarly the $T_{A-M}$ is also included in (b) for samples annealed at 873 K, which also exhibited a constant transformation temperature of $\sim 280$ K regardless of the level of cold work.

Figure 4.8. Effect of prior cold work on the thermal transformation behaviour of Ti-50.5at%Ni annealed at 623 K

As seen in (a), $T_{M-R}$ dropped by only $\sim 10$ K when the level of cold work was increased from 35% to 95% for all annealing temperature. Excessive cold working to beyond 95% caused no change to this transformation temperature. On the other hand, $T_{R-A}$ remained constant for all levels of cold work. However, lowering the annealing temperature from 723 K to 673 K caused $T_{R-A}$ to increase by more than 10 K at all levels of cold work.

It is seen in (b) that $T_{A-R}$ for each annealing temperature remained constant regardless of the level of cold work. However, lowering the annealing temperature from 823 K to 623 K caused $T_{A-R}$ to increase by as much as 40 K. Meanwhile, $T_{R-M}$ drastically decreased as the level of cold work increased for all samples annealed at below 723 K, with the
maximum effect achieved from the sample annealed at 623 K. The effect is much reduced for annealing temperatures above 773 K.

![Graph showing the effect of cold working on transformation temperatures](image-url)

Figure 4.9. Effect of cold working on transformation temperatures: (a) heating transformations and (b) cooling transformations

Figure 4.10 summarises the effect of annealing temperature with respect to the level of cold working on transformation temperatures. This is in fact a reconstruction of the data from the same experiments as for Figure 4.9, to reveal a different aspect of the relationships. It is seen that $T^{R-M}$ decreased rapidly with annealing temperature for samples cold-worked for more than 67%. Samples cold worked for 95% and 170%
exhibited similar effects. However, samples cold worked for 35% and 15% showed much reduced dependences on annealing temperature. Meanwhile, $T^{A-R}$ exhibited similar dependence on annealing temperature for all levels of cold work. The $T^{M-R}$ and $T^{R-A}$ shifted to lower temperatures as the level of cold work increased, but their changes with respect to annealing temperature remained similar.

![Figure 4.10. Effect of annealing temperature on transformation temperatures of Ti-50.5at%Ni cold worked to different levels](image)

Figure 4.11 shows the effect of annealing temperature and cold work on the enthalpy change of transformations. The $\Delta h^{\text{Total Heating}}$ and $\Delta h^{\text{Total Cooling}}$ represent the summation of all transformation latent heats measured on the heating and cooling, respectively. In all cases, the latent heat on heating is always slightly higher than that on cooling. Figure (a) shows that the latent heats decreased as the annealing temperature decreased. The decrease is more drastic from samples cold-worked at higher elongation percentages. Figure (b) shows that the effect of cold work percentage on the latent heat is nearly negligible when the annealing temperature was above 823 K. The influence of cold work with respect to the anneal temperature only takes effect when the samples were annealed at below 773 K, where the latent heat continued to decrease as the cold work increased.
4.1.3 Effect of Cold Work Percentage on Mechanical Behaviour

Figure 4.12 shows the tensile deformation behaviour of the cold worked samples after annealing at four different temperatures. The testing temperature was 313 K for all samples. In general, annealing in this temperature range may produce good pseudoelasticity for this alloy system. Figure 4.12 (a) shows the deformation behaviour of wire samples annealed at 773 K. All samples show a similar critical stress for the forward stress-induced transformation at ~280 MPa except for the sample deformed by 15% cold work. This sample was deformed at ~200 MPa. The stresses for the reverse transformation also remained at similar levels for all samples cold worked for more than 35%, but no pseudoelasticity was achieved for the sample cold worked by 15%.

Figure 4.12 (b) shows the deformation behaviour of the samples annealed at 723 K. The samples showed a progressive increase in the stress for inducing the forward transformation with increasing the level of cold work from 15% to 67%. Above this cold work level, the samples showed a similar stress for inducing the martensitic transformation, at ~350 MPa. Once again, no pseudoelasticity was observed for the sample cold worked by 15%.

Figure 4.12 (c) shows the deformation behaviour of the samples annealed at 673 K. These specimens show an obvious progressive increase of $\sigma_{\text{fwd}}$ with respect to the level of cold work. The sample cold worked by 15% showed a partial pseudoelasticity. Figure 4.12 (d) shows the deformation behaviour of the samples annealed at 623 K. The 15% cold-worked sample showed a good pseudoelastic strain recovery with only 1.5%
permanent strain. At the meantime, the Lüders type characteristics of the samples seem to have been weakened.

Figure 4.12. Tensile deformation behaviour of Ti-50.5at%Ni at 313 K after annealing at: (a) 773 K, (b) 723 K, (c) 673 K and (d) 623 K

Figures 4.13 summarises the effect of the level of cold work on the critical stresses for the forward and the reverse stress-induced martensite transformations. As seen in (a), the stresses for the forward transformation remained nearly the same at ~170 MPa for fully annealed samples (above 873 K) regardless of the amount of cold work. Similarly, annealing at 823 K and 773 K produced almost negligible influence of the cold work on the transformation stress, and increase of stress level as compared to fully annealed samples is mainly due to the anneal temperature effect. The effect of cold work percentage is more obvious when the annealing temperature is below 723 K. As seen in the figure, the critical stress of the sample cold worked by 67% is ~130 MPa higher than that of the sample cold worked by 15% for annealing at 723 K. However, the increase of this critical stress stabilised at 67% of cold work. Further increase of cold work percentage did not cause the critical stress to increase further. This implies that
increasing the level of cold work to beyond 67% produces no advantage on improving the yield strength of the alloy after annealing at this temperature. Nevertheless, further lowering of annealing temperature to 623 K allows the alloy to deform via stress-induced transformation at ~550 MPa when the level of cold worked was 170%. This stress is ~330 MPa above that of the sample cold worked by 15%.

Similar phenomenon is also observed for the critical stress for the reverse transformation, as seen in Figure 4.13 (b). Annealing at the high temperature of 773 K erased all influence of the cold work on the critical stress for the reverse transformation. Annealing at 673 K and below was found to be effective in preserving the increase of yield strength with respect to the increase of cold work percentage.

![Figure 4.13. Effect of cold work on the critical stress for inducing martensitic transformation: (a) forward transformation and (b) reverse transformation](image)

Figure 4.14 shows the effect of annealing temperature on the critical stresses for stress-induced martensitic transformation with respect to the level of cold work. The figure is based on the experimental data shown in Figure 4.12. Figure 4.14 (a) shows the effect on the forward transformation and figure (b) shows the effect on the reverse transformation. As seen in (a), the stress for the forward transformation decreased continuously with increasing annealing temperature and stabilised at above 850 K. This stabilisation was reached at the same temperature for all samples regardless of the level of cold work. This implies that increasing the cold work percentage did not affect the recrystallisation temperature. As seen in figure (b), cold working by 15% produced very minimal improvement to the yield strength and consequently poor pseudoelasticity. Cold working between 35% and 95% seems to be the optimum range for enhancing
shape memory behaviour of this alloy. Excessive cold working to beyond 170% is seen to be unnecessary.

![Graph showing effect of annealing temperature on critical stress for inducing martensitic transformation](image)

Figure 4.14. Effect of annealing temperature on the critical stress for inducing martensitic transformation: (a) forward transformation and (b) reverse transformation

In practical use, the stress hysteresis of pseudoelastic behaviour is also a concern. A narrow hysteresis is not desirable for certain applications with fluctuating load or temperature, where the stability of the deformation can be jeopardised by a small change of external load or temperature. On the other hand, a wide hysteresis may not be good for other applications that require cyclic loading and high actuation reversibility. Proper combination of cold work percentage and annealing temperature would allow modification of the stress hysteresis for specific functions.

![Graph showing effect of cold work percentage on pseudoelastic stress hysteresis](image)

Figure 4.15 shows the effect of cold work percentage on the pseudoelastic stress hysteresis of the alloy after anneal at different temperatures. It is evident that the stress hysteresis increased continuously with increasing the level of prior cold work for all anneal temperature. In the case of annealing at 623 K, a typical temperature for optimising pseudoelasticity, the hysteresis may increase by 43% when increasing the level of cold work from 35% to 170%. The minimum hysteresis achieved was 160 MPa for the sample cold worked by 35% and annealed at 623 K.
Figure 4.15. Effect of cold work percentage on pseudoelastic stress hysteresis of Ti-50.5at%Ni

Figure 4.16 shows the effect of annealing temperature on the pseudoelastic stress hysteresis of the alloy. It is seen that for low levels of cold work (e.g., 35%) the stress hysteresis increased continuously with increasing annealing temperature. For samples cold worked to high levels (e.g., 95% and 170%), the stress hysteresis exhibited a maximum at intermediate annealing temperatures. The maximum hysteresis achieved was 300 MPa for the sample cold worked by 170% and annealed at 723 K.

Figure 4.16. Effect of annealing temperature on pseudoelastic stress hysteresis of Ti-50.5at%Ni
4.1.4 Discussion

Cold working is generally carried out to improve pseudoelasticity of near-equiatomic NiTi alloys. Sometimes this process is also conducted with the purpose of changing the shape and dimension of a material product or a particular component. Cold work introduces high densities of dislocations and structural defects in the matrix. These defects generate internal stresses, strengthen the matrix and subsequently affect the martensitic transformations. Annealing after cold working negates the effect of cold working, through recovery and recrystallisation. Recrystallisation is normally done to restore the neutral matrix for maximum shape memory effect. Recovery alters dislocation and defect structures to different levels. Correspondingly, the martensite transformation is also altered to respond to this microstructure change. Result shown in Figure 4.2 illustrates that the suppression of transformation temperatures from the cold work effect in Region II is progressively relaxed over the increase of annealing temperature for recovery. Recovery is also a time-dependent process, thus a prolonged heating would also improve the relief of internal stresses and promote grain growth, which eventually restores the neutral matrix [168].

Whereas the principles of these effects are common knowledge, little attention has been given in the literature to quantify the effect of cold work on martensitic transformation related deformation behaviour of NiTi. Most studies reported in literature analyse the effect of cold work on thermal transformation behaviour [168-173]. Recently, multistage thermal transformation behaviour of cold-worked alloys has captured interest [171, 174], partly due to the similar behaviour observed from aged Ni-rich alloy [108, 121, 149-151]. Chang et al. [174] reported a 4-stage martensite transformation observed from a cold-rolled and partially annealed Ti-50.0at%Ni. This phenomenon was rationalised based on inhomogeneous grain size distribution caused by cold rolling.

4.1.4.1 Effect of Partial Anneal on Thermal Transformation Behaviour

Transformation temperatures are generally suppressed by the presence of defects introduced by cold working, and consequently the forward B2→B19’ martensitic transformation may be preceded by B2→R transformation, and similarly the reverse B19’→B2 transformation may be preceded by B19’→R transformation, as evident in Figures 4.6-4.8.
The introduction of random structural defects by cold work also widens transformation temperature intervals as observed in Figures 4.6-4.9, where the height of transformation peaks is reduced and the transformation interval widened as the cold work percentage increases. This has also been well reported in the literature [135, 136, 147, 175]. The widened transformation interval implies that transformation is inhomogeneous, manifesting in the delay of the finish or the advance of the start of the transformation. This is evident in Figure 4.17, where the transformation interval increases with increasing plastic deformation due to advance of A_s while A_f remain nearly constant. This is due to the mechanical inhomogeneity of the matrix that makes local transformation to happen at actually different temperatures, i.e. effectively to break the whole transformation peak into many small overlapping peaks, thus broadening the “apparent interval”. This interval is not a true interval described by thermodynamics. Thermodynamic interval is caused by the increase of elastic energy $\Delta E_{el}(f_m)$ during the process of transformation in a local unit. When a martensite variant starts to form, it creates $\Delta E_{el}(f_m=0)$ elastic energy in the specific form of joules per gram (J/g). At the maturity of this variant, it creates $\Delta E_{el}(f_m=1)$ (J/g) elastic energy. The total elastic energy this variant has accumulated during its growth from the beginning to the end may be expressed as $E_{el} = \frac{1}{f_m=0} \int \Delta E_{el}(f_m) df_m$. The transformation temperature at the start of the transformation is affected by $\Delta E_{el}(f_m=0)$ and that at the end of the transformation is determined by $\Delta E_{el}(f_m=1)$. Therefore, the transformation interval is determined by $\Delta E_{el}(f_m=1) - \Delta E_{el}(f_m=0)$.

Although it is clear that the “apparent interval” widens as the cold work percentage increases, there is no direct evidence to prove that the thermodynamic interval is also widened. If the defect does make the thermodynamic interval wider, the start of the forward transformation $M_s$, may not be affected (no change of $\Delta E_{el}(f_m=0)$), but will delay the finish of the transformation $M_f$ (increase of $\Delta E_{el}(f_m=1)$). Similarly for the reverse, it will lower the start temperature $A_s$, and will not affect the finish $A_f$, as seemingly seen in Figure 4.17. However, Figures 4.6-4.8 show that the $M_s$ decreases as the cold work percentage increases. This implies that the increase of the temperature interval is mainly contributed by the inhomogeneity of the transformation. In regard of the inhomogeneous transformation, a DSC peak is actually composed of many small transformation peaks. Each is a microscopic thermodynamic process itself. That implies
that a transformation interval is a cumulative of these small and unresolved peaks. This observation also suggests that the martensite formed first on cooling (at $M_s$) will revert back to austenite last (at $A_f$). Similarly, the last martensite formed (at $M_f$) will first revert to austenite (at $A_s$).

![Figure 4.17. Effect of plastic deformation on reverse martensitic transformation peak of a Ti-50.6at%Ni alloy [175]](image)

### 4.1.4.2 Effect of Partial Anneal on Mechanical Behaviour

It is seen in Figures 4.13 and 14 that the critical stresses to induce the martensitic transformation in the partially annealed samples increase with increasing the level of prior cold work, and the increases are more prominent for low annealing temperatures. For the fully recrystallised samples, i.e. those annealed at above 873 K, the effect of prior cold work is totally eliminated. The increase of the stresses presented in Figure 4.13 cannot be fully ascribed to the effect of the partial anneal on the metallurgical conditions of the matrix, because it is known that the actual stress for inducing martensite is also a function of the testing temperature relative to $T^{R-M}$. This means that:

$$\sigma^{fwd}(T) = \sigma^{fwd}_{mech} + \sigma^{fwd}_{therm}(T)$$

(4.1)

where $\sigma^{fwd}_{mech}$ is the mechanical resistance to the deformation of stress-induced martensitic transformation of the matrix and $\sigma^{fwd}_{therm}(T)$ is the thermodynamic resistance to the phase transformation caused by temperature deficit ($T - T^{R-M}$). However the temperatures in Figures 4.9 and 4.10 are for $R \rightarrow M$ ($T^{R-M}$), while the stress induced
transformation is $A \rightarrow M (A \rightarrow M)$. To take this into account, $T^{A-M}$ can be estimated using the free energy relation [176]:

$$T^{A-M} = \frac{\Delta H^{A-R} + \Delta H^{R-M}}{\frac{\Delta H^{A-R}}{T^{A-R}} + \frac{\Delta H^{R-M}}{T^{R-M}}}$$

(4.2)

Using the measured values of $\Delta H^{A-R} = 6.5 \text{ J/g}$ and $\Delta H^{R-M} = 13.5 \text{ J/g}$ for this alloy system, $T^{A-M}$ for the 67% cold-worked samples are calculated and the results are shown in Figure 4.18 with respect to anneal temperature. The calculated $T_s^{A-M}$ represents the estimated starting temperature of $B2 \rightarrow B19'$ transformation (which is thermodynamically prohibited in the samples), $T_s^{A-R}$ is the measured starting temperature of $A \rightarrow R$ transformation and $T_s^{R-M}$ is the measured starting temperature of the $R \rightarrow M$ transformation. The measured peak temperatures of $B2 \rightarrow B19'$ (peak $T^{A-M}$) and $R \rightarrow B19'$ (peak $T^{R-M}$) are also included in the figure for comparison. Similarly, the measured starting temperatures of $B2 \rightarrow B19'$ ($T_s^{A-M}$) from fully recrystallised samples are also included, and are artificially connected with the calculated $T_s^{A-M}$ curve. This illustrates the validity and continuity of the calculation with the actual measurement.

Using the interpolated value of $T_s^{A-M}$, $\sigma_{\text{therm}}^{\text{fwd}}(T)$ can be estimated using the Clausius-Clapeyron relation. Taking the $\frac{d\sigma}{dT} = 5 \text{MPa/K}$ [177], the calculated values of $\sigma_{\text{therm}}^{\text{fwd}}(T) = (T - T_s^{A-M}) \frac{d\sigma}{dT}$ for the samples annealed at different temperatures are shown in Figure 4.19. The measured values of $\sigma_{\text{fwd}}^{\text{fwd}}(313K)$ are also included in the figure for comparison. Following equation 4.1, the difference between $\sigma_{\text{therm}}^{\text{fwd}}(313K)$ and $\sigma_{\text{therm}}^{\text{mech}}$ is obviously the mechanical resistance of the matrix to deformation of the stress-induced martensitic transformation, $\sigma_{\text{mech}}^{\text{fwd}}$. It is evident that $\sigma_{\text{therm}}^{\text{fwd}}$ decreased with increasing annealing temperature, which is obviously caused by the increase of $T_s^{A-M}$ with increasing anneal temperature (Figure 4.18), whereas $\sigma_{\text{mech}}^{\text{fwd}}$ remained practically constant at ~40 MPa.
Figure 4.18. Interpolated value of $T_s^{A-M}$ for 67% cold-worked samples annealed at different temperatures.

Figure 4.19. Effect of annealing temperature on thermodynamic stress $\sigma_{\text{therm}}^{fwd}$ for inducing B2-B19’ martensitic transformation in Ti-50.5at%Ni.
Figure 4.20 shows comparison of the measured $\sigma_{\text{fwd}}$ and the calculated $\sigma_{\text{fwd}}$ as functions of the percentage of cold work for three annealing temperatures. It is evident that $\sigma_{\text{fwd}}$ followed the trend of $\sigma_{\text{fwd}}$ for all the three conditions, implying that variation of the transformation stress is mostly caused by variation of the transformation temperature. It is also evident that $\sigma_{\text{mech}}$ remained practically constant with respect to percentage of cold work for all the three annealing temperatures.

In conclusion, the increase of critical stress for transformation by the increase of cold work percentage is mainly due to the suppression of transformation temperature, particularly $\text{B2} \rightarrow \text{B19}'$. Meanwhile, the mechanical resistance $\sigma_{\text{mech}}$ remains constant and is not influenced by the annealing temperature or cold work percentage.
4.2 Martensite Stabilization

It is known that deformation stabilizes martensite [32, 135, 137, 138, 178]. The deformation induced martensite stabilisation effect manifests as the increase of reverse transformation temperature of the deformed martensite, produced via either stress-induced martensitic transformation or martensite reorientation [41, 42]. Quantitative characterisation of this effect is of critical importance for design and application of SMAs. Previous analyses on this effect have all been carried out using fully recrystallised samples. However, in many applications the alloys produced for shape memory effect or pseudoelasticity are partially annealed, yet no work has been done to characterise the deformation induced martensite stabilisation effect of partially annealed NiTi. This experiment determines the magnitude of the stabilisation effect from alloys annealed at different temperatures. The intention of the analysis is to provide a knowledge base of the susceptibility of near-equiatomic NiTi alloys to the stabilization effect. Such understanding is of direct relevance to the application of these alloys. The sample used in this analysis was Ti-50.2at%Ni wire with the initial diameter of 1.4 mm.

4.2.1 Thermal Transformation Behaviour

Figure 4.21 shows the thermal transformation behaviour of the Ti-50.2at%Ni alloy annealed at different temperatures between 623 K and 923 K for 1 hour. The amount of the prior cold work is 30%. Figure 4.22 shows the peak temperatures of the forward and reverse transformations with respect to annealing temperature. These two figures are similar to Figures 4.1 and 4.2, respectively, but their transformation temperatures are different due to different alloys used. Additionally, the reverse transformation on the heating of this Ti-50.2at%Ni alloy always exhibited a single-stage B19’→B2 transformation, as compared to the Ti-50.5at%Ni alloy that involved a two-stage B19’→R→B2 transformation as the annealing temperature is lowered to below 773 K. Comparing the peak transformation temperatures of $T^{M-M}$ or $T^{M-A}$ of the fully recrystallised samples from both alloys shows that the Ti-50.2at%Ni is higher than the Ti-50.5at%Ni by ~15 K. However, their thermal hystereses are nearly the same of about 30 K. This observation agrees well with the literature [144], which relates the composition-dependence of the transformation temperature.
Figure 4.21. Thermal transformation behaviour of Ti-50.2at%Ni as annealed at different temperatures for 1 hour.

Two horizontal dashed lines are drawn in Figure 4.22 to indicate the testing temperatures used for tensile deformation. The 293 K was approached by initially cooling the sample to below 200 K and then reheated to 293 K prior to deformation. This was to ensure that the sample was fully in the state of martensite phase. On the other hand, the 313 K was approached by heating the sample to above 350 K and subsequently cooled down to 313 K prior to deformation. This was to ensure that the sample was in the state of austenite phase or R-phase. This setting allows the deformation to be carried out from two different modes: the stress-induced martensitic transformation at 313 K and the martensitic reorientation at 293 K.
4.2.2 Mechanical Behaviour

Figure 4.23 shows the deformation behaviour of the samples after annealing at different temperatures. The samples were deformed at 313 K. As indicated in Figure 4.21, samples annealed at low temperatures were in R phase state whereas those annealed at high temperatures were in austenitic state prior to loading; thus the deformation proceeded via stress-induced B2→B19’ or R→B19’ transformations. For the samples annealed at high temperatures (>823 K), the initial deformation exhibited stress-induced B2→R transformation starting at 75 MPa, as indicated by the arrow in the figure, and B2→B19’ transformation starting at ~1.7% strain via Lüders-type deformation. For the samples annealed at low temperatures (<773 K), the deformation began with a linear elastic deformation and then proceeded via stress-induced B2→B19’ transformation over a Lüders-type stress plateau. For all the samples the deformation proceeded to 6.3%, just beyond the end of the stress plateau. It is evident that the critical stress for inducing the martensitic transformation increased with decreasing annealing temperature. It is also noted that with decreasing annealing temperature (and increasing critical stress for inducing the transformation at the given temperature), spontaneous pseudoelastic recovery upon unloading also increased.
Figure 4.23. Tensile deformation behaviour of Ti-50.2at%Ni at 313 K

Figure 4.24 shows the deformation behaviour of the samples at 293 K. The samples were all in martensitic state at the start of the deformation and the deformation proceeded via martensite reorientation. It is seen that the two recrystallised samples annealed at above 873 K showed Lüders-type deformation over the stress plateau whereas others showed a uniform deformation of the reorientation with increasing stress.

Figure 4.25 shows the effect of annealing temperature on the critical stresses for the forward stress-induced transformations at 313 K (Figure 4.23) and for martensite reorientation at 293 K (Figure 4.24). It is seen that both stresses increased with decreasing annealing temperature in the range below the recrystallisation temperature. The increase of stress for inducing the transformation is much more rapid than that for martensite reorientation. At above the recrystallisation temperature the critical stress showed little dependence of the annealing temperature.
Figure 4.24. Tensile deformation behaviour of Ti-50.2at%Ni at 293 K

Figure 4.25. Effect of annealing temperature on critical stress for transformation deformation of Ti50.2at%Ni
4.2.3 Transformation Behaviour after Deformation

Figure 4.26 shows DSC measurements of the transformation behaviour of the samples deformed at 313 K (Figure 4.23). All samples were in the unloaded state, and had been cooled in liquid nitrogen prior to the DSC measurement. All measurements started with heating from room temperature. For each sample, the endothermic transformation at the higher temperature is the first reverse transformation of the deformed martensite, denoted B19$'$→B2*. Following that the sample experienced a complete normal thermal transformation cycle, exhibiting either the B2↔B19$'$ transformation cycle for the two fully recrystallised samples (873 K and 923 K) or the transformation cycle of B2→R→B19$'$ martensitic transformations on cooling and the B19$'$→B2 reverse transformation on the second heating for the un-recrystallised samples. The transformation behaviour in the complete thermal transformation cycle after the first reverse transformation is practically the same as the transformation behaviour of the undeformed sample for each annealing temperature (Figure 4.21). The occurrence of B19$'$→B2* at a higher temperature above that for B19$'$→B2 demonstrates the martensite stabilisation effect. It is evident that the extent of stabilisation, as indicated by the temperature difference between B19$'$→B2 and B19$'$→B2*, increased with increasing annealing temperature.
Figure 4.26. Thermal transformation behaviour of Ti-50.2at%Ni after deformation via stress-induced martensitic transformation at 313 K

Figure 4.27 shows DSC measurements of the transformation behaviour of the samples deformed at 293 K (Figure 4.24). Practically the same effects of partial anneal on the martensite stabilisation were observed for the case of deformation via martensite reorientation.
Figures 4.28 and 4.29 show the effect of annealing temperature on the transformation temperatures for the two sets of samples deformed at 313 K and 293 K, respectively. The $T_{M-A^*}$ is the peak temperature of the first reverse transformation of the deformed martensite and the $T_{M-A}$ is the peak temperature of the reverse transformation of the thermally induced self-accommodating martensite on the second heating. It is seen that for both sets of samples, $T_{A-M}$, $T_{A-R}$, $T_{R-M}$ and $T_{M-A}$ are all similar to those of the undeformed samples, as presented in Figure 4.22. In contrast, $T_{M-A^*}$ shows clear increase from $T_{M-A}$. 
Figure 4.28. Effect of annealing temperature on transformation temperatures of Ti-50.2at%Ni deformed via stress-induced transformation at 313 K

Figure 4.29. Effect of annealing temperature on transformation temperatures of Ti-50.2at%Ni deformed via martensite reorientation at 293 K

Figure 4.30 compares the difference of reverse transformation temperatures for both samples deformed via stress-induced martensitic transformation (deformed at 313 K) and martensite reorientation (deformed at 293 K). It is seen that the increase of $T^{M-A^*}$ is
slightly higher for the samples deformed via stress-induced transformation than those deformed via martensite reorientation. This increase is more significant for samples annealed at temperature higher than 800 K. On the other hand, $T^{M-A}$ for both samples remained almost identical for all annealing temperatures. The $T^{M-A}$ of the undeformed sample extracted from Figure 4.22 is also included in this figure. This temperature represents the first cycle of thermal reverse transformation. It is seen that $T^{M-A}$ for all conditions remain similar.

![Graph](image)

Figure 4.30. Comparison of the reverse transformation temperatures of Ti-50.2at%Ni after deformation via stress-induced martensitic transformation and martensite reorientation for samples annealed at different temperatures

Figure 4.31 shows the temperature interval between $T^{M-A*}$ and $T^{M-A}$ as a function of the annealing temperature for the two deformation modes of stress-induced martensitic transformation and martensite reorientation. It is seen that the two different deformation modes showed practically identical effect on stabilisation and that the stabilisation effect increased with increasing annealing temperature. The maximum amplitude of the stabilisation effect is $\sim 30$ K for the samples annealed at 923 K and the minimum is practically zero for the samples annealed at 623 K.
4.2.4 Discussion

The increase of the magnitude of the stabilisation effect with increase of annealing temperature may be rationalised on the basis of matrix resistance to plastic deformation. The matrix of the samples annealed at higher temperatures contain fewer dislocations and are softer compared with those annealed at lower temperatures, and are thus expected to be more susceptible to internal plastic deformation during the transformation deformation. In contrast, the samples annealed at lower temperatures contain more dislocations and therefore lesser new defects are expected to be generated during the transformation deformation.

These defects impose a mechanical resistance to the reverse shape change accompanying the reverse transformation of the reoriented martensite, thus cause the first reverse transformation to occur at a higher temperature [41, 42, 178]. The reverse transformation on the subsequent cycle of heating involves only the transformation of self-accommodated martensite, which is free from the constraint of the deformation induced defects, thus experiences no stabilisation effect.

These observations have direct implications to the design of shape memory apparatuses. Near-equiatomic NiTi alloys exhibit the best shape memory effect and two-way memory trainability when annealed at just above the crystallisation temperature, but
these materials experience the most severe deformation-induced stabilisation, retarding
the shape recovery. This effect must be taken into account in design of shape memory
apparatuses. In contrast, annealing at between 623~723 K produces near-equiaxial
NiTi of optimum pseudoelasticity. These alloys experience negligible stabilisation
effect, which is an advantage for design using these alloys.
SURFACE OXIDATION AND TITANIUM DEPLETION

As discussed in chapter 2, excessive surface oxidation will impair the shape memory properties of NiTi alloys. Industrial production of bulk NiTi alloys often involves solution treatment to above 1073 K, particularly for ageing precipitation process. In laboratory practices, oxidation is avoided or minimised by running the treatment either in vacuum or in inert gas environment. However, hot working process is normally carried in air environment for economical reasons. In this case, where sometimes the need and the cost require justification or optimisation, the complete and correct information and understanding regarding the effect of surface oxidation on shape memory behaviours are critical. This chapter focuses on the influences of heat treatment environment, temperature and time on surface oxidation of NiTi alloys. Transformation and deformation behaviours of the alloys are then analysed to determine the quantitative effect of the oxidation. The alloy used was Ti-50.5at%Ni, in the form of wire of 1.5 mm in diameter.

5.1 Surface Oxidation

It is known that titanium is reactive to oxygen at elevated temperatures, particularly above 873 K. The oxide layer formed in the ambient is normally very thin and serves as a protective layer preventing further oxidation whilst imposing no influence on the mechanical performance of the alloy. However, heat treatment at above 873 K for prolonged periods encourages the formation of thick and non-protective oxide layer on the metal surface.
5.1.1 Initial Sample Condition

Figure 5.1 shows the thermal transformation behaviour of the Ti-50.5at\%Ni alloy used. The as-received sample is shown in curve (a). The original wire was in cold-worked state, and exhibited very weak $B_2 \rightarrow R$ and $R \rightarrow B_{19}'$ transformations. Curve (b) represents a sample recrystallised at 873 K in argon for 1 hour. The sample showed a single step of $B_2 \leftrightarrow B_{19}'$ transformation. The hysteresis is 32 K and enthalpy change is $\sim 22$ J/g.

![Diagram of thermal transformation behaviour of Ti-50.5at\%Ni](image)

Figure 5.1. Thermal transformation behaviour of Ti-50.5at\%Ni

Figure 5.2 shows SEM images of the wire cross section for both samples. It is seen that the surface condition of both wires is practically the same, with negligible thickness of oxide layer. This indicates that the as-received wire has not been oxidised and the heat treatment at 873 K in argon has prevented oxidation of the sample. The inset in (a) shows an enlarged general view of the interior of the sample, revealing the presence of some small polygonal inclusions in the original matrix. These inclusions are TiC formed during smelting of the alloy [unpublished work].
5.1.2 SEM Observation on Surface Oxidation

5.1.2.1 Effect of Heat Treatment Temperature on Oxidation

Figure 5.3 shows SEM images of the cross sections of samples annealed at different temperatures in air for 1 hour. It is evident of the progressive growth of oxidation thickness on the surface of the samples as the heat treatment temperature increases. Exposure to air for 1 hour at 973 K produced negligible oxidation. The oxide did not form a continuous layer, but appears to be non-uniform and penetrating into the interior at intermittent locations, implying that oxidation occurred preferentially at surface defects. Increasing the temperature to 1073 K led to the formation of a continuous and uniform oxide layer of ~15 μm thickness. At 1173 K, the oxidation appears to have generated separate layers of different structures, with the outer layer being the original oxide and the underneath layer being a composite of two phases. At 1223 K the underneath layer has evolved into a continuous ring of ~20 μm in thickness.
Figure 5.3. Cross section view of Ti-50.5at%Ni heat treated in air for 1 hour at: (a) 973 K, (b) 1073 K, (c) 1173 K and (d) 1223 K

Figure 5.4 shows the effect of prolonged heating time at different temperatures in air for 24 hours. It is seen that a prolonged exposure to air at 873 K may allow oxidation to occur, which was not seen for short heating time of 1 hour (Figure 5.3). Elevating the treatment temperature to 1073 K caused an increase in the extent of oxidation. The thickness of the oxide is obviously greater than that after heating for 1 hour (Figure 5.3(b)). Increasing heat treatment temperature to 1173 K caused severe oxidation. The oxidised layer has also evolved into a composite of two phases, as seen in Figure 5.4(d).

Figure 5.4. Cross section view of Ti-50.5at%Ni heat treated in air for 24 hours at: (a) 873 K, (b) 973 K, (c) 1073 K and (d) 1173 K
5.1.2.2  Effect of Heat Treatment Time on Oxidation

The results shown above indicate that oxidation occurs vigorously at high temperatures, particularly above 1173 K. Solution treatment for this alloy in industrial production is normally carried out at temperatures above 1100 K. Therefore, it is necessary to characterise the time-dependence of the oxidation temperature above this level. Figure 5.5 shows SEM images of wire cross sections after treatment in air at 1223 K for different times. It is seen that at this temperature obvious oxidation has occurred at times as short as 15 minutes. The growth of the oxide layer was relatively slow and steady when the exposure time was less than 2 hours. After 4 hours of heat treatment, there appears to be a sudden increase in the rate of oxidation, as evidenced by the drastically increased oxidation layer thickness. This was found to coincide with severe cracking of the surface oxide, apparently due to build-up of excessive compressive stresses. An example of this severe oxide cracking was captured in Figure 5.5(g). Cracking of the surface oxide layer losses its protection and exposes the fresh metal below the surface to air again, encouraging a continued inward growth of oxidation. It is also evident that most growth occurred to the inner composite layer. Increasing the exposure time at this temperature led to rapid continuous growth of the oxidised layer.
5.1.2.3 Prevention of Surface Oxidation in Argon Environment

Figure 5.6 shows images of two samples heat treated in argon for 1 hour at (a) 1173 K and (b) 1223 K. It is evident that no obvious oxidation occurred on the surfaces.

Figures 5.7 shows SEM images of wires heat treated at 1223 K in argon environment for different times. It is evident that the surface oxidation is negligible even after 24 hours of heat treatment. The surface conditions of all samples are very similar. This
implies that heat treatment in Argon environment was good in preventing oxidation even at 1223 K for prolonged time.

Figure 5.7. Cross section view of Ti-50.5at%Ni heat treated at 1223 K in argon for different periods

5.1.2.4 **Structure of the Oxidised Surface**

As seen above, excessive surface oxidation caused the formation of multi-layer structures on the surface, including the outer oxide layer and the composite layer underneath. EDS analysis was carried out to determine the compositions of these phases. Figure 5.8 shows SEM images revealing the details of the oxidised layers and EDS analysis of the various phases. The sample was heat treated at 1223 K in air for 4 hours. It is seen that the oxidised surface contained actually three distinctive layers, the outer layer, the middle layer of a duel phase composite, and a thin inner layer. Micrograph (b) shows details at the interface between the middle (composite) layer and then outer layer. Micrograph (c) shows the detailed view of the interface between the composite layer and the interior of the sample, in which the thin inner layer is clearly seen.
The outer layer is a uniform, single phase layer. EDS analysis shows that it contains ~99.8at%Ti (excluding oxygen). This layer is obviously pure titanium oxide (TiO$_2$). In this sample, the thickness of this oxide is ~50 µm.

The middle layer contains about equal amounts of the two phases. The dark phase appears to be continuous. EDS analysis indicates that it contains ~96at%Ti and 4at%Ni (excluding oxygen). The SEM image (Figure 5.8(b)) also demonstrates clearly that this dark phase is a continuation of the outer surface into the interior of the sample. This dark phase is identified to be TiO$_2$. The small amount of Ni is believed to be from the white phase due to the proximity between the two phases. The white phase appears to be isolated islands uniformly distributed within the matrix of the dark phase. EDS analysis indicates that it contains ~94at%Ni and 6at%Ti. This phase is identified to be solid solution of Ti in Ni, denoted Ni(Ti). This phase is obviously the residual of the NiTi alloy after the oxidation.

The inner layer forms thinly beneath this second layer with a thickness of about 5 µm, as seen in micrograph (c). The thickness of this thin layer remains nearly constant at 5 µm for all treatment times. EDS analysis reveals that it contains 24~27at%Ti and 73~76at%Ni. This layer is identified to be TiNi$_3$. 
The far interior of the sample remained the initial alloy composition of Ti-50.5at%Ni, as confirmed by EDS analysis. Similar pattern of composition variation was observed on other samples as well, but with different thickness of the middle layer. Small and dispersed particles are also visible in the matrix, with some appearing in the TiNi$_3$ layer too. These particles are pre-existing in the original alloy, as seen in Figure 5.2, and are not product of the heat treatment.

5.1.2.5 **The Growth of Oxidised Layer**

Figure 5.9 shows the growth of the surface layers with respect to exposure time for samples heat treated at 1223 K in air. Since the oxide layer on samples heat treated in argon was negligible, their data are not included in this figure. The TiO$_2$ layer was only
measureable from samples heat treated in air for up to 4 hours treatment, after which the TiO$_2$ layer cracked off the surface and no further TiO$_2$ layer was created. It is seen that the TiO$_2$ layer thickness increased with increasing heat treatment time in air and reached a maximum value of 50 μm after 4 hours. The TiNi$_3$ layer remained at a constant thickness of ~5 μm since its appearance during the entire history of treatment time. This observation is identical for both the air and argon environments. The growth of composite layer thickness for the samples treated in air showed progressive increase with time. There appears to be an incubation time with a relatively low growth rate till 2 hours, after which the growth rate suddenly increased. This is believed to be due to the cracking of the surface TiO$_2$ layer, which had served as a barrier layer for oxidation. After 24 hours the thickness of the composite layer has increased to ~0.5 mm, leaving only 0.5 mm diameter of core, as compared to the original diameter of 1.5 mm.

Figure 5.9. The growth of oxide-affected layers with respect to heat treatment time for samples heat treated in air at 1223 K

Figure 5.10 shows the effect of heating temperature on the composite layer thickness for samples heat treated in air. For the samples treated in air for 1 hour, the composite layer thickness increased with increasing temperature very mildly, reaching a maximum value of 25 μm at 1223 K. However, prolonged exposure for 24 hours allowed the composite layer to grow even at 873 K. There appear to be a “take-off” temperature of ~1100 K, at which the growth rate of the composite layer becomes drastically increased. On the
other hand, no physical change of surface condition was observed from samples heat treated in argon in both extreme heat treatment temperature and time. This implies that the argon environment was good in preventing surface oxidation.

Figure 5.10. Effect of heat treatment temperature on thickness of the composite layer

5.1.3 Effect of Oxidation on Transformation Behaviour

5.1.3.1 Transformation Behaviour

Figures 5.11 and 5.12 show the transformation behaviour of the Ti-50.5at\%Ni alloy after heat treatment at different temperatures for one hour in air and argon, respectively. The samples were pre-cut into disks of $\phi 1.50 \times 1.50$ mm, with an average mass of 20 mg, prior to the heat treatment. Thus oxidised layers were formed on all surfaces. It is seen that transformation temperatures of the samples remained largely unchanged but the size of the thermal peaks decreased continuously with increasing the treatment temperature for both heat treatment atmospheres.
Figure 5.11. Transformation behaviour of Ti-50.5at%Ni heat treated in air for 1 hour

Figure 5.12. Transformation behaviour of Ti-50.5at%Ni heat treated in argon for 1 hour
Figures 5.13 and 5.14 show the transformation behaviour of the samples heat treated at different temperatures for 24 hours in air and argon, respectively. The effect is similar to that shown in Figures 5.11 and 5.12, except that the reduction of the transformation heat with increasing heat treatment temperature is much more severe. In comparison, the reduction of transformation heat for the samples treated in air is more pronounced than those treated in argon at any given temperature, as expected. The transformation temperatures remain unaffected.

Figure 5.13. Transformation behaviour of Ti-50.5at%Ni heat treated in air for 24 hours

Figure 5.15 shows the transformation behaviour of the samples after heat treatment in air at 1223 K for different times. Similar to the effects of heat treatment temperature, increasing heat treatment time at 1223 K diminished the transformation enthalpy change progressively. After 24 hours of heat treatment in air, no transformation was detected. The transformation temperatures still remained unchanged.
Figure 5.14. Transformation behaviour of Ti-50.5at%Ni heat treated in argon for 24 hours

Figure 5.15. Transformation behaviour of Ti-50.5at%Ni heat treated at 1223 K in air
Figure 5.16 shows the transformation behaviour of the samples heat treated at 1223 K in argon for different times. The evolution of the transformation behaviour over time is very similar to the case of heat treatment in air shown above. The transformation temperatures remained unchanged and the transformation enthalpy decreased with treatment time.

Heat treatments have also been conducted at 1073 K and 1173 K in air and in argon atmospheres. The observations are consistent with the results presented above. The DSC curves of these samples are not shown to avoid redundancy.

**5.1.3.2 Effect of Oxidation on Transformation Enthalpy Change**

Figure 5.17 shows the effect of heat treatment temperature on the transformation enthalpy change of the samples treated for 1 and 24 hours in argon and air. It is seen
that the enthalpy change of the alloy in the original annealed state is ~22 J/g. Heating in air for 1 hour caused the enthalpy change to decrease moderately, but with increased margin at higher heat treatment temperatures. At 1223 K, the highest temperature tested, the enthalpy change is reduced to 12.5 J/g, 57% of the original value. Heating in argon showed slightly milder effect.

Heating for 24 hours in air caused much more measurable effect. The enthalpy change decreased rapidly with increasing heat treatment temperature. The sample heat treated at 1173 K showed an enthalpy change of 4 J/g, only 18% of the original value. The sample heat treated at 1223 K exhibited no detectable transformation, as evident in Figure 5.15. The samples heat treated in argon for 24 hours also showed significant and continuous decreases of the enthalpy change with increasing heat treatment temperature, although to a less extent compared to the samples treated in air. Unlike treatment in air, the sample heated in argon at 1223 K still exhibits transformation, with the enthalpy change of 11.5 J/g, reduced to 52% of the original value.

![Figure 5.17. Effect of heat treatment temperature on transformation enthalpy change](image_url)

Figure 5.17. Effect of heat treatment temperature on transformation enthalpy change

Figure 5.18 shows the effect of heat treatment time on transformation enthalpy change at three different treatment temperatures of 1073 K, 1173 K and 1223 K. The open symbols represent samples treated in argon and the closed symbols represent samples treated in air. It is seen that the samples showed similar trend of continuous decrease of enthalpy change at all three heat treatment temperatures. The decrease is more rapid...
initially and then the rate of reduction decreased with prolonged heating. It is evident
that at all three temperatures the decrease of the enthalpy change is greater for the
samples treated in air than in argon, as expected. It is also obvious that prolonged
heating at 1173 K in air caused greater reduction of enthalpy change than heating at
1223 K in argon. In addition, it is also seen that the decrease of enthalpy seems to
stabilise after 14 hours of heating in argon for all three temperatures, but it continues to
decrease for samples treated in air at above 1173 K.

The relative reduction of the enthalpy change after 24 hours of heating for all the
samples is summarised in Table 5.1.

Table 5.1. The relative reduction of the enthalpy change after 24 hours of heating

<table>
<thead>
<tr>
<th>Heat Treatment Temperature</th>
<th>Air</th>
<th></th>
<th>Argon</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H$ (J/g)</td>
<td>Reduction (%)</td>
<td>$\Delta H$ (J/g)</td>
<td>Reduction (%)</td>
</tr>
<tr>
<td>As-annealed</td>
<td>21.8</td>
<td>-</td>
<td>21.8</td>
<td>-</td>
</tr>
<tr>
<td>1073 K</td>
<td>12.8</td>
<td>42</td>
<td>14.6</td>
<td>34</td>
</tr>
<tr>
<td>1173 K</td>
<td>4.1</td>
<td>81</td>
<td>12.8</td>
<td>42</td>
</tr>
<tr>
<td>1223 K</td>
<td>0</td>
<td>100</td>
<td>11.7</td>
<td>47</td>
</tr>
</tbody>
</table>

Figure 5.18. Effect of heat treatment time on transformation enthalpy change
5.1.3.3 Effect of Oxidation on Transformation Temperature

Figure 5.19 shows the effect of heat treatment temperature on transformation temperatures of samples heat treated in argon and air environments for 1 hour. It is seen that all transformation temperatures remain unchanged, except a slight drop of $M_f$ and $A_s$ after heat treatment to above 1173 K. This implies that 1 hour exposure in the argon and air within this range of temperature did not affect the thermal transformation behaviour of this alloy.

![Figure 5.19. Effect of heat treatment temperature on transformation temperatures for samples heat treated in argon and air for 1 hour](image)

Figure 5.20 shows the effect of heat treatment temperature on transformation temperatures of samples heat treated in argon and air environments for 24 hours. It is seen that heating the samples to above 1000 K causes the $A_f$ and $M_s$ to drop mildly but drastic drop of $A_s$ and $M_f$. The magnitudes of these temperatures drop in both argon and air conditions are similar. This indicates that the change of thermal transformation behaviour due to heat treatment temperature is similar in both environments. The suppression of $M_f$ implies the delay of the finishing of the forward transformation and the lower temperature of $A_s$ implies the advance of the reverse starting temperature. This phenomenon indicates that the phase transformations may have occurred non-uniformly within the matrix.
Figure 5.21 shows the effect of heat treatment temperature on transformation intervals of samples heat treated for 1 hour and 24 hours in both argon and air environments. Samples treated for 1 hour show only minimal increase of transformation temperature interval as the treatment temperature increases. Samples treated for 24 hours show very drastic increase of temperature interval when heating to above 1073 K. The increase of temperature interval is mainly due to the decrease of $M_f$ and $A_s$. In all cases, the temperature interval on the reverse transformation is greater than the forward transformation.

![Transformation Temperatures](image)

Figure 5.20. Effect of heat treatment temperature on transformation temperatures for samples heat treated in argon and air for 24 hour

Figure 5.22 shows the effect of heat treatment time on transformation temperatures for samples heat treated at 1223 K in argon and air. The open symbols are for samples heat treated in argon and the closed symbols are for samples heat treated in air. Transformation temperatures for samples treated in air were only detectable and measurable up to 14 hours of treatment time. It is seen that $A_f$ and $M_s$ remain nearly unchanged even after 24 hours of heat treatment in both argon and air environments. On the other hand, $A_s$ and $M_f$ continue to drop as the treatment time is prolonged. However, $M_f$ of sample heat treated in air showed only a slight drop after 2 hours of heat treatment and then remained nearly constant as the time was further prolonged.
Figure 5.21. Effect of heat treatment temperature on transformation temperature interval for samples heat treated in argon and air for 1 hour and 24 hours.

Figure 5.22. Effect of heat treatment time on transformation temperatures.

Figure 5.23 shows the effect of heat treatment time on transformation temperature interval of samples heat treated at 1223 K in argon and air. The temperature intervals continue to increase as the treatment time increases for both forward and reverse transformations. This increase is mainly due to the decrease of $M_f$ and $A_s$ over the treatment time, as evidenced in Figure 5.22. Samples heat treated in argon shows wider temperature interval than the samples heat treated in air. It is also seen that the
temperature interval in the reverse transformation is wider than the forward transformation. Samples treated in air show nearly similar increase of intervals on both forward and reverse transformations for short treatment time but the reverse transformation interval begin to increase wider than the forward transformation after 8 hours of treatment.

Figure 5.23. Effect of heat treatment time on transformation temperature interval

5.2 Titanium Depletion

It has been found that heat treatment in air at elevated temperatures not only causes oxidation to the alloy on the surface but also Ti depletion in the matrix. This is easy to understand given that the oxidation occurs preferentially with Ti to form TiO$_2$.

The experimental evidences presented in the previous section demonstrate that heat treatment in air causes drastic reduction to the transformation enthalpy change. This may be easily attributed to the loss of material due to surface oxidation. However, transformation enthalpy of samples treated in argon also decreased, though the extent of oxidation in these samples is much less than that of the samples treated in air. This is attributed to depletion of titanium in the matrix.
5.2.1 Composition Profile

To verify the phenomenon of titanium depletion, EDS analyses were carried out on these samples to quantify the composition profile across the sample cross sectional area. The electron beam was set at 20 kV and the working distance was set at 16 mm. This setting produced an electron beam size of about 10 nm, which yields an estimated spatial resolution of ~1 μm for composition analysis. This resolution was practically good to avoid spots overlapping and ensure sufficient size of the spot for reliable composition analysis. The compositions were only analysed from the non-oxidised region of the wire cross section area. The first spot was ~10 μm from the inside edge of the surface oxide. This is to avoid the electron beam from hitting the oxide layer. A maximum of 12 EDS spots were identified starting from the region near the surface towards the core of the sample, as illustrated in Figure 5.24. A narrower gap between spots was made near the surface region since it was expected that this region will experience more depletion activity than the core. Knowing that the core will experience much lesser effect of Ti depletion, the remaining EDS spots towards the core from which the composition has reached uniformity were not analysed.

5.2.1.1 Effect of Heat Treatment Temperature on Titanium Depletion

Figures 5.24 shows the locations of EDS measurement on the cross sections of three samples heat treated in air for 1 hour at different temperatures. Negligible depletion of Ti is seen in the sample treated at 873 K, even at near the surface. Heat treatment at 1073 K in air caused the Ti to deplete to below 49at% at near the surface but the depth of penetration of the depletion zone is less than 50 μm. The sample treated at 1223 K showed sharp Ti depletion to 46.7at% at near the oxide layer and a much deeper affected region.

Figure 5.25 shows the Ti concentration profiles across the sectional area of five samples which have been heat treated for 1 hour in air at between 873 K and 1223 K. It is seen that the Ti content in the interior of the alloy remained unchanged at the original level of Ni-49.5at%Ti. The Ti content dropped rapidly at near the surface. The Ti depletion is minimal for samples heat treated at 973 K and below. At above 1073 K, both the margin of Ti depletion and the depth of the Ti depleted zone increased remarkably. The horizontal dotted line (MT), indicates the practical minimum limit of Ti composition in the matrix for the alloy to exhibit the B2-B19’ martensitic transformation.
Figure 5.24. EDS analysis of Titanium concentration in samples heat treated in air for 1 hour at: (a) 873 K, (b) 1073 K and (c) 1223 K

Figure 5.25. Titanium composition profiles for samples heat treated for 1 hour in air

Figure 5.26 shows two examples of EDS measurements from samples heat treated in argon for 1 hour at 1073 K and 1223 K. Since the oxide layer for all samples treated in
argon is negligible, the last EDS spot near the surface was identical for all samples, which was ~ 10 μm from the surface. It is seen that although the thickness of oxide layer formed on the surface is similar on all samples, more severe and deeper penetration of Ti depletion has happened on the sample that was heat treated at the higher temperature.

Figure 5.26. Titanium composition gradient for samples heat treated in argon for 1 hour at: (a) 1073 K and (b) 1223 K

Figure 5.27 shows the composition profiles of all samples after heat treated in argon for 1 hour. Samples heat treated at 1073 K and below showed minimal depletion of titanium. Samples treated at above 1173 K showed measurable Ti depletion near the surface. Both the margin of Ti depletion and the depth of Ti depleted zone are much less compared to the case of heat treatment in air.

Figure 5.27. Titanium composition profile for samples heat treated for 1 hour in argon
Figure 5.28 shows EDS measurements of three samples treated in air for 24 hours at different temperatures. Figure 5.29 shows the composition profiles of all samples after heat treatment in air for 24 hours. Severe depletion of titanium is produced in all the samples. The single arrows indicate the positions of the interface between the oxidised layer and the parent metal. The double arrows indicate the penetration depth of the Ti-depletion zone. It is seen that both the level of Ti depletion and the penetration depth of the depletion increase with increasing the heating temperature. For the sample heat treated at 1223 K the Ti-depleted zone has penetrated through the entire sample thickness. This is consistent with the observation that no transformation detected by DSC of this sample, as shown in Figure 5.13.

Figure 5.28. Titanium composition gradient for samples heat treated in air for 24 hour at: (a) 873 K, (b) 1073 K and (c) 1173 K

Figure 5.30 illustrates the growth of the Ti-depleted zone thickness with respect to treatment temperature, as summarised from Figure 5.29. The oxide-related layer shown in this figure includes the surface layer of TiO₂, the composite and TiNi₃ layers. It is seen that the Ti-depletion zone grows concurrently with the growth of oxide-related layer. For the sample treated at 1223 K, the entire sample was consisted of thick oxide layer of ~450 μm and a 600 μm Ti depleted core with < 48at%Ti.
Figure 5.29. Titanium composition profile for samples heat treated in air for 24 hours

Figure 5.30. Titanium depletion affected zone from samples heat treated in air for 24 hours

Figure 5.31 shows two examples of the EDS measurements from samples treated in argon for 24 hour at different temperatures. Figure 5.32 shows the composition profile for all the samples. It is seen that the drop of Ti content is not so abrupt in the region near the surface, as compared to the samples treated in air. However, the width of the Ti depleted zone to below 49at% extended to nearly 300 μm from the surface for the
sample treated at 1223 K. A measureable depletion is also seen in samples treated at 1173 K and 1073 K. Negligible depletion is seen in samples treated at below 973 K. This Ti depletion pattern is in good agreement with the decrease of transformation enthalpy shown in Figure 5.14. For example, DSC measurement has shown that the transformation enthalpy of the sample treated at 1223 K has decreased to around 50% of the original value. Meanwhile, EDS analysis indicates that nearly half of the area has been depleted to below 49at% of its Ti content, which caused the matrix to lose its martensitic transformation. This implies that the decrease of transformation enthalpy is largely due to the depletion of Ti in the matrix.

Figure 5.31. Titanium composition gradient for samples heat treated in argon for 24 hours at: (a) 1073 K and (b) 1173 K

Figure 5.32. Titanium composition profile for samples heat treated for 24 hours in argon
Figure 5.33 shows the Ti content at the interface of oxide-related layer and core (parent metal), as function of heat treatment temperature for both the samples heat treated in air and in argon. It is seen that the content of Ti at the interface decreases continuously as the treatment temperature increases. The pattern of this decrease is similar in all cases but with greater effect on sample treated in air. This is largely due to the continuous growth of oxide-related layer in sample treated in air with respect to the increase of temperature. It is also seen that prolonged exposure time caused the Ti near the interface to deplete much more in both environments. However, exposure in air for 1 hour caused more severe depletion than exposure in argon for 24 hours. This may be attributed to the formation of much thicker oxide layer on the sample exposed in air as compared to the sample in argon.

![Figure 5.33. Ti content at the interface of core and oxide layer as function of treatment temperature from samples treated in air and argon environments](image)

Figure 5.34 compares the effect of treatment temperature on the depth of the Ti-depletion zone for samples treated in air and argon. The curves indicate the depth of penetration where the Ti content has been depleted to below 49at%. This depth measurement also includes the thickness of the oxidation-affected layers (TiO$_2$, composite and TiNi$_3$ layers) formed at the surface on samples heat treated in air. Thicker oxide is expected to induce greater depletion of Ti in the remaining core, which is translated into lower Ti content at the interface, as seen in Figure 5.33. Heating the sample at below 1173 K for only 1 hour either in air or argon produced only shallow
depletion penetration. However, a much deeper penetration is achieved when the samples are heated at above 1173 K. On the other hand, a prolonged time of exposure to 24 hours has allowed the Ti to deplete into much deeper zone even at 973 K, in both air and argon environments. This implies that the Ti depletion is a continuous process over the time.

Figure 5.34. The depth of the Ti depleted zone as function of treatment temperature from samples treated in air and argon environments

It is seen that the whole volume of the sample that was heated in air for 24 hours has been depleted to below Ti-49at%, meanwhile the depletion penetration depth for the sample heated in argon is only ~300 μm. However, if the thickness of the oxide-related layer is excluded from the penetration depth measurement of the sample treated for 24 hours in air, the width of Ti-depletion zone for this sample is nearly similar to the sample treated in argon for the same period. This observation is demonstrated by the dotted curve in Figure 5.34. This dotted curve represents the width of Ti-depletion after excluding the thickness of the oxide-related layer for sample heat treated in air for 24 hour. A slightly greater penetration depth from the sample treated in air is expected due to the effect of thick oxide-related layer.
5.2.1.2 Effect of Heat Treatment Time on Titanium Depletion

Figure 5.35 shows four examples of the EDS measurements from samples treated in air at 1223 K for different times. The measurement was conducted up to the interface between the oxidised layer and the parent metal. Figure 5.36 shows the composition profile for all the samples. It is seen that the affected area due to Ti depletion grows progressively as the exposure time increases. For heat treatment at 1223 K, even the short period of 15 min is enough to cause abrupt depletion of Ti at near the surface.

![Figure 5.35. Titanium composition gradient for samples heat treated in air at 1223 K for: (a) 15 minutes, (b) 2 hours, (c) 8 hours and (d) 24 hours](image)

Figure 5.37 shows four examples of the EDS measurements from samples treated in argon at 1223 K for different times. Figure 5.38 shows the composition profile for all the samples. It is seen that due to the negligible thickness of oxide formed on the surface, the depletion of Ti is not so abrupt in the region near the surface. The worst case is from the sample treated for 24 hours. It only caused the Ti to deplete to 47.6at%. Even so, the depth of the depletion zone for this sample is relatively large, which is ~300 μm.
Figure 5.36. Titanium composition profile for samples heat treated in air at 1223 K for different time

Figure 5.37. Titanium composition gradient for samples heat treated in argon at 1223 K for: (a) 15 minutes, (b) 2 hours, (c) 8 hours and (d) 24 hours
Figure 5.38. Titanium composition profile for samples heat treated in argon at 1223 K for different time.

Figure 5.39 shows the Ti content of the matrix at near the core and oxide layer interface as function of heat treatment time for both the samples heat treated in air and in argon. It is seen that the Ti content decreases abruptly during the initial hour and then stabilises as the time increases. The measured value of Ti content from samples treated in air is always lower than the samples treated in argon. Higher values of Ti content is seen in samples heated in air for 4 and 8 hours as compared to samples treated for shorter time is probably due to invariant EDS spot location. This happened because the depletion of Ti at the interface of oxide and the parent metal is very abrupt, and so slight mis-positioning of spot from the interface may yield a difference EDS reading. This phenomenon is easily avoided from samples heated in argon because the thickness of oxide layer formed on the surface is practically similar.

Figure 5.40 shows the effect of treatment time on the depth of the Ti-depletion zone for samples treated in air and argon. The penetration depth continues to increase as the time increases, with higher effect on samples treated in air as compared to samples treated in argon. Similar to the phenomenon presented in Figure 5.34, if the oxide thickness is removed from the penetration depth measurement, the width of the depletion zone for samples treated in air is illustrated by the dotted curve shown in Figure 5.40. It is seen that the depth of Ti depletion beyond the oxide layer is very similar for both treatment
environments. This implies that the Ti depletion penetration depth is not dictated by the thickness of the oxide layer.

Figure 5.39. Ti content at the interface of core and oxide layer as function of time from samples treated at 1223 K

Figure 5.40. The depth of the Ti-depleted zone as function of time from samples treated at 1223 K
5.3 Deformation Behaviour

Oxidation and Ti depletion caused by high temperature treatment are expected to affect the mechanical behaviour of the alloy. Figure 5.41 shows the tensile deformation behaviour of Ti-50.5at%Ni at 296 K. The sample was initially annealed at 873 K in argon for 1 hour. The SEM image of the cross-section of the wire sample is shown in Figure 5.2. DSC measurement of the transformation behaviour is shown in the Figure 5.1. Heat treatment at this condition does not cause significant oxidation or Ti depletion. Since the testing temperature was above the \( M_s \) temperature of 287 K, the deformation proceeded with stress-induced martensitic transformation at \( \sim 95 \) MPa. The deformation exhibits a clear Luders type deformation and yields about 7% of global strain upon reaching the end of the stress plateau. \( \sim 6.2\% \) of residual strain was recorded when the sample was unloaded just before the “take-off” of the apparent plastic deformation.

![Figure 5.41. Deformation behaviour of recrystallised Ti-50.5at%Ni in tension at 296 K](image)

5.3.1 Effect of Heat Treatment Temperature on Deformation Behaviour

Figure 5.42 and 5.43 show the tensile deformation behaviour of the samples heat treated at different temperatures for 1 hour in air and argon, respectively. The deformation was carried out in air at room temperature of about 296 K. It is seen that the critical stress for the stress-induced transformation increases with increasing heat treatment temperature. All samples were deformed to 15% without fracture, except the sample heat treated at 1223 K, in both air and argon. None of the samples from either set
showed pseudoelasticity at this testing temperature. Deformation beyond the transformation stress plateau showed similar behaviour among all the samples. The two samples heat treated at 1223 K in argon and in air fractured before reaching the end of the stress plateau in brittle mode.

Figure 5.42. Deformation behaviour of samples heat treated for 1 hour in air

Figure 5.43. Deformation behaviour of samples heat treated for 1 hour in argon
Since oxidation and titanium depletion are time dependent processes, it is therefore necessary to quantify the influence of long time treatment on mechanical behaviour. Figure 5.44 and 5.45 show the tensile deformation behaviour of the samples heat treated at different temperatures for 24 hours in air and argon, respectively. Prolonged heating at 1173 K caused the samples to fracture before reaching the end of stress plateau in both cases of treatment in argon and air.

Figure 5.44. Deformation behaviour of samples heat treated for 24 hour in air

Figure 5.45. Deformation behaviour of samples heat treated for 24 hour in argon
Figure 5.46 shows the effect of treatment temperature on the critical stress for inducing the forward martensitic transformation for both treatments in argon and air. It is seen that the critical stress for inducing the transformation increases progressively with increasing heat treatment temperature for both atmospheres. The increment of the stress is greater for the heat treatment for 24 hours than for 1 hour, as expected.

It is also interesting to note that there appears to be negligible difference between the samples treated in air and in argon for both treatment durations except that samples heat treated in air for 24 hours at 1173 K and 1223 K fractured before the start of stress-induced martensitic transformation. In this regard, no critical stress for transformation is recorded from these fractured samples, as marked in the figure. The fracture is probably due to the influence of thick and brittle oxidation layers formed on samples heat treated at 1173 K and 1223 K for 24 hours, as shown in Figure 5.10. The thickness of oxidation layers for samples treated for 1 hour in air at all temperatures and those treated for 24 hours at below 1073 K is less than 50 μm. This suggests that the presence of thin oxide layers of less than 50 μm did not affect the stress-induced martensitic transformation behaviour of the alloy. This implies that the increase of stress is more likely influenced by the width of Ti depletion zone.

Figure 5.46. Effect of treatment temperature on forward transformation stress

Figure 5.47 shows the effect of treatment temperature on the forward martensitic transformation strain for both treatments in argon and air. It is seen that the strain
increased continuously with treatment temperature. A slightly higher magnitude of strain is measured from samples annealed in air as compared to samples annealed in argon at all temperatures for the 1 hour heat treatment. Strain measurement at 1223 K for this set of samples is not available because the sample fractured before reaching the end of transformation. Similarly, strain measurements from samples heat treated for 24 hours are only available for treatment temperature at below 1073 K.

5.3.2 Effect of Heat Treatment Time on Deformation Behaviour

Figure 5.48 and 5.49 show the deformation behaviour of samples treated at 1223 K for different periods in air and argon, respectively. For the heat treatment in air, all samples treated longer than 1 hour fractured before reaching the end of stress plateau. Samples treated for more than 14 hours show no sign of stress-induced transformation. Samples heat treated in argon show clear stress-induced martensitic transformation, and the stress for the transformation increased progressively with increasing treatment time.
Figure 5.48. Deformation behaviour of samples treated at 1223 K in air

Figure 5.49. Deformation behaviour of samples treated at 1223 K in argon

Figure 5.50 shows the effect of heat treatment time on the critical stress for transformation for samples treated at 1223 K in argon and air. It seen that the critical stress increases rapidly in the initial heat treatment period of less than 1 hour. Samples treated in air for more than 2 hours fractured before the start of the stress-induced martensitic transformation. Therefore, no critical stress record is available for these samples. For treatment in argon, all samples survived the deformation until the
martensitic transformation plateau. It is seen that its stress increases at a slower rate thereafter in the entire time range tested.

![Graph showing stress vs. time for Ti-50.5at%Ni heat treated at 1223 K]

**Figure 5.50.** Effect of heat treatment time on forward transformation stress

### 5.4 Discussion

#### 5.4.1 Formation Mechanisms of Multilayer Surface by Oxidation

Oxidation of near-equiatomic NiTi occurs by the selective reaction of titanium with oxygen to form TiO$_2$. This is dictated by the fact that the formation free energy of TiO$_2$ is much lower than that of NiO. Table 5.2 summarises the formation free energies of several Ni and Ti compounds at 1023 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ti</th>
<th>Ni</th>
<th>TiNi</th>
<th>TiNi$_3$</th>
<th>NiTi$_2$</th>
<th>TiO$_2$</th>
<th>NiO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G$ (kJ/mol)</td>
<td>-</td>
<td>-</td>
<td>-156</td>
<td>-319</td>
<td>-220</td>
<td>-759</td>
<td>-147</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>4.54</td>
<td>8.91</td>
<td>6.45</td>
<td>~7.8</td>
<td>~7.4</td>
<td>4.25</td>
<td>6.67</td>
</tr>
<tr>
<td>Molar vol. (cm$^3$)</td>
<td>10.6</td>
<td>6.6</td>
<td>16.5</td>
<td>28.7</td>
<td>20.9</td>
<td>18.8</td>
<td>11.2</td>
</tr>
</tbody>
</table>

As presented in section 5.1.2, oxidation induces the formation of complex multiple layers on the surface of NiTi, including the outer layer of TiO$_2$, the middle layer of TiO$_2$
Ni(Ti) composite, the inner layer of TiNi\textsubscript{3} and the Ti-depleted region in the NiTi matrix. Evolution of these multi-layers over time is demonstrated in Figures 5.5 and 5.8.

The process of oxidation initiates by the formation of TiO\textsubscript{2} on the surface. The consumption of Ti (and the consequent enrichment of Ni) in the matrix at the surface induces the outward diffusion of Ti and the inward diffusion of Ni. This process may be schematically expressed as in Figure 5.51 (Stage I).

In this illustration, atomic percentages of Ti and Ni are expressed as relative percentages of the two elements only, thus the percentage of Ti in TiO\textsubscript{2} is considered 100%. In this condition, the Ti content of the matrix at the interface with TiO\textsubscript{2} is below 50at\%, as expressed by the solid concentration curve. The dotted curve represents the enrichment of Ni content in the matrix corresponding inversely to the depletion of Ti. Theoretically, Ti atoms that have been leached out from the matrix are converted into TiO\textsubscript{2}. Therefore, it is practically convenient to consider that the molar number of the TiO\textsubscript{2} layer is equivalent to the molar number of Ti-depletion region.

Continuation of the oxidation process will eventually deplete Ti at the interface to \(~\text{25at\%}\). This will trigger the conversion of the NiTi alloy into TiNi\textsubscript{3} underneath the TiO\textsubscript{2} layer, as illustrated in Stage II. The chemical process of the oxidation may be expressed as:

\[
3\text{NiTi} + 2\text{O}_2 \rightarrow \text{TiNi}_3 + 2\text{TiO}_2 \quad \Delta G_{\text{reaction}} = -1370 \text{ kJ/mol} \quad (5.1)
\]

This reaction indicates that the depletion of Ti stabilises at 25at\%. Further Ti supply for oxidation requires the outward diffusion of Ti from deeper matrix through the TiNi\textsubscript{3} layer formed, instead of a total depletion of Ti at the interface of the matrix and the TiO\textsubscript{2}. 

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Illustration in Stage II implies that the formation of the new phase of TiNi₃ is only started when the TiO₂ layer reaches a certain thickness. Continued oxidation in Stage II thickens both the TiO₂ and TiNi₃ layers. This condition is illustrated in Figure 5.52 (Stage III). During this stage, the thickness expansion occurs by the inward movement of the left boundaries for both layers.

As their thicknesses increase, reaction (5.1) for the formation of TiO₂ at the TiO₂/TiNi₃ interface becomes more and more difficult, because of the increased diffusion distances for the oxygen through TiO₂ and titanium through TiNi₃. The lack of supply of free Ti
atoms at the interface will eventually force the oxidation to take a different route via the decomposition of TiNi$_3$, as expressed in reaction (5.2):

$$ TiNi_3 + O_2 = 3Ni(Ti) + TiO_2 \quad \Delta G_{\text{reaction}} = -440 \text{ kJ/mol} \quad (5.2) $$

This reaction is thermodynamically less favoured than reaction (5.1) but permissible. This reaction results in the in-situ conversion of TiNi$_3$ into a mixture of Ni(Ti) (a solid solution of Ti in Ni) and TiO$_2$. This mechanism creates a new composite layer of Ni(Ti) and TiO$_2$ between the TiNi$_3$ layer and the surface layer of TiO$_2$, as illustrated in Figure 5.52 (Stage IV).

![Figure 5.52](image)

Figure 5.52. Schematic illustration of the formation of composite layer by oxidation
As the oxidation continues, the thickness of composite layer continues to grow from the consumption of TiNi$_3$ layer. This causes the outer boundary of the TiNi$_3$ layer to be pushed inward, thus reduces its thickness. A reduced TiNi$_3$ thickness will re-trigger reaction (5.1), thus thickening the TiNi$_3$ layer again. This implies that during this stage the TiNi$_3$ layer has reached a dynamic equilibrium of a given thickness and moves continuously inwards while the composite layer expands, as observed experimentally and summarised in Figure 5.9. It is also obvious that during this stage the growth of the TiO$_2$ layer has completely ceased. This is also consistent with the experimental evidences observed above.

5.4.2 Morphology of the Surface Layers

As demonstrated in Figures 5.51 and 5.52, the growth of TiO$_2$ and TiNi$_3$ layers in the early stage of oxidation is governed by reaction (5.1). This reaction has a volume expansion of 34%. This increase of volume implies that the TiNi$_3$ and TiO$_2$ layers are under compressive stress. According to reaction (5.1), the relative thicknesses (volume fractions) of the TiNi$_3$ and TiO$_2$ layers are estimated to be 43:57. This thickness ratio seems to agree with the experimental observation during the early stage of oxidation, as shown in Figure 5.53. This thickness estimation assumes that the radius difference between the two layers is negligible since their thicknesses are very thin (less than 20 μm), as compared to the radius of the specimen (0.75 mm).

![Figure 5.53. Early stage development of oxidation with the formation of TiNi$_3$ and TiO$_2$](image)
The formation of the composite layer is governed by reaction (5.2). This reaction also has a volume expansion of 34%, implying that the composite layer is also under severe compressive stress. Based on reaction (5.2), the relative volume fractions of TiO$_2$ and Ni(Ti) are estimated to be 49:51. Image analysis of the SEM micrograph shown in Figure 5.54 determines that the volume ratio of TiO$_2$ to Ni(Ti) in the composite area is 44:56, as summarised in Table 5.3. This ratio is a slight overestimation of TiO$_2$ relative to Ni(Ti). This is believed to be due to simultaneous occurrence (to a small extent) of reaction (5.1) within the composite layer during Stage III.

![Image analysis for composition ratio of Ni(Ti):TiO$_2$ in the composite layer](image)

Figure 5.54. Image analysis for composition ratio of Ni(Ti):TiO$_2$ in the composite layer

<table>
<thead>
<tr>
<th>Black hole included</th>
<th>Black hole excluded</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black holes</td>
<td>TiO$_2$ (dark phase)</td>
</tr>
<tr>
<td>Black holes</td>
<td>TiO$_2$ (black phase)</td>
</tr>
<tr>
<td>3.2</td>
<td>54.4</td>
</tr>
<tr>
<td></td>
<td>56.2</td>
</tr>
</tbody>
</table>

Table 5.3. Volume fractions of phases in the composite zone

### 5.4.3 Effect of Oxidation on Thermal Transformation Behaviour

#### 5.4.3.1 Transformation Temperature

As evident in Figure 5.19, all transformation temperatures remain practically constant over the heat treatment temperature range for samples treated for 1 hour in either environment. This implies that the composition of the alloy is largely unaffected by the oxidation reaction occurred on the surface. However, for prolonged heating for 24 hours, as shown in Figure 5.20, $M_f$ and $A_s$ are found to decrease drastically when heated.
to above 1073 K, in both environments. It is also evident in Figures 5.21 and 5.23 that the transformation temperature interval widens with increasing temperature or time, respectively.

Close examination shows that the widening of $\Delta T_{\text{forward}}$ and $\Delta T_{\text{reverse}}$ is due to the decreases of $M_f$ and $A_s$, respectively, while $M_s$ and $A_f$ remain constant. This implies that the transformations are not homogeneous where a delay is encountered on the finishing of forward transformation and an advance is encountered on the starting of reverse transformation. The delay of $M_f$ and the advance of $A_s$ are obviously caused by the enrichment of Ni content in the Ti-depleted zone by the oxidation reaction, which caused the decrease of transformation temperatures locally within the zone.

The magnitude of these temperatures decrease is directly related to the amount of Ti depleted from the matrix. This is evident from EDS analysis shown in Figures 5.33 where the depletion of Ti at the interface of core and oxide layer continued to increase as the heat treatment temperature increased, and correspondingly translated into similar trend of temperature decrease for $M_f$ and $A_s$, as observed in Figure 5.20. Similarly, the continuous increase of Ti depletion at the interface of core and oxide layer as a function of heat treatment time, as shown in Figure 5.39, shows the same effect of $M_f$ and $A_s$ decrease (Figure 5.20).

### 5.4.3.2 Transformation Heat

Formation of the oxide at surface layers, which exhibit no martensitic transformations, is expected to reduce the apparent latent heat of the transformation measured by DSC. The decrease of the transformation latent heat, as summarised in Figures 5.17 and 5.18 corresponds well to the reduction of the volume fraction of the parent alloy that survived the oxidation, as shown in Figures 5.9 and 5.10. The volume of the remaining parent NiTi alloy is measured from the cross section SEM images shown in Figures 5.4 and 5.5, for the samples treated in air. However, the decrease of transformation latent heat is only partly due to the formation of oxide. The transformation latent heat of the samples heat treated in argon also decreased significantly, for example; by 47% after heating for 24 hours at 1223 K as compared to the original sample. SEM observation shows clearly that the thickness of the oxide formed on the surfaces of these samples

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was negligible. The growth of the surface layers with heat treatment time or temperature was also negligible.

In this regard, the reduction of transformation latent heat is also attributed to the depletion of Ti from the matrix. Figures 5.34 and 5.40 show that significant thickness of core outer region from samples heat treated in argon have depleted its Ti content to below 49at%, regardless of the negligible oxide formed on its surface. The depletion of Ti inversely increases the atomic percentage of Ni in the matrix. $\Delta H$ (and $M_s$) decreases with increasing Ni from 50at%, due to lowering of the degree of B2 ordering. When Ni>52at%, $M_s$ is too low and $\Delta H$ is too small, thus transformation disappears. Total $\Delta H$ reduction is from both the disappearance of the transformation in regions where Ni>52at% and from regions where there is still transformation but Ni is more than the original concentration.

The same effect should also be expected for the air samples. This means that for the air samples the latent heat reduction is caused by two reasons: loss of volume due to the formation of oxide-related layers and the depletion of Ti within the core.

### 5.4.4 Estimation of Transformation Enthalpy

The decrease of $\Delta H$ due to oxidation and Ti depletion can be estimated based on physical measurement of the oxide-related layers formed on the surface (Figure 5.9 & 5.10) and the depth of Ti-depletion zone (Figure 5.34 & 5.40). Estimation of the survived alloy that is able to exhibit martensitic transformation can be schematically illustrated in Figure 5.55. The sample was in the form of bar with ~2 mm of length and 1.5 mm of diameter. During the heat treatment all surfaces were subjected to oxidation-related effect.

The “shell” represents the oxide-related layer that includes TiO$_2$, composite and TiNi$_3$ phases. The “dead zone” represents the alloy matrix with depleted Ti to below 49at%. These “shell” and “dead zone” layers do not exhibit martensitic transformation. The “core” is the central region that maintains the composition at >Ti-49at% and is assumed as the only volume that can exhibit martensitic transformation. The limit of Ti-49at% is slightly higher than the reported value for this alloy to exhibit martensitic transformation [144]. However this value is practically sensible after considering the
gradual change of composition at the interface of “core” and “dead zone”. With this consideration, a superficial finite interface boundary between the “core” and the “dead zone” regions can be defined.

Figure 5.55. Schematic illustration of the samples cross section area showing the layers of “shell”, “dead zone” and “core”

Based on the measured thicknesses of the oxide oxide-related layers and the Ti-depleted zone, the volume of the core can be estimated, as tabulated in Table 5.4 and 5.5, for samples for 1 hour and 24 hours, respectively. Since the samples were in the form of bar, the “dead zone” and “shell” volumes also include the layers at both ends of the bar.

Table 5.4. Estimation of core volume for sample treated in air and argon for 1 hour

<table>
<thead>
<tr>
<th>Temp</th>
<th>Core Volume (Treatment in Air)</th>
<th>Core Volume (Treatment in Argon)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diameter (mm)</td>
<td>Volume (%)</td>
</tr>
<tr>
<td>873 K</td>
<td>1.50</td>
<td>100</td>
</tr>
<tr>
<td>973 K</td>
<td>1.50</td>
<td>100</td>
</tr>
<tr>
<td>1073 K</td>
<td>1.46</td>
<td>93</td>
</tr>
<tr>
<td>1173 K</td>
<td>1.44</td>
<td>89</td>
</tr>
<tr>
<td>1223 K</td>
<td>1.35</td>
<td>75</td>
</tr>
</tbody>
</table>
Table 5.5. Estimation of core volume for sample treated in air and argon for 24 hours

<table>
<thead>
<tr>
<th>Temp</th>
<th>Core Volume (Treatment in Air)</th>
<th>Core Volume (Treatment in Argon)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diameter (mm)</td>
<td>Volume (%)</td>
</tr>
<tr>
<td>873 K</td>
<td>1.50</td>
<td>100</td>
</tr>
<tr>
<td>973 K</td>
<td>1.42</td>
<td>86</td>
</tr>
<tr>
<td>1073 K</td>
<td>1.25</td>
<td>61</td>
</tr>
<tr>
<td>1173 K</td>
<td>0.84</td>
<td>22</td>
</tr>
<tr>
<td>1223 K</td>
<td>0.00</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 5.56 compares the correlation between the percentages of “core” volume with the measured transformation enthalpy change of the respective samples. It is seen from samples heat treated for 1 hour that the measured enthalpy is lower than the estimated volume of the survived “core”. This suggests that the thickness of the “dead zone” is actually thicker than the estimated value based on the limit of Ti-49at%. One possibility is that the diffusivity of titanium atoms may have disrupted the long-range ordered structure of B2 phase. This disruption may impose additional internal resistance for the martensitic transformation to occur, typically nearby the “dead zone” region. On this consideration, the thickness of the “dead zone” layer should be taken at higher value, thus the estimated decrease of transformation enthalpy with respect to the decrease of “core” volume can be more accurate. On the other hand, it is seen that the estimation of “core” volume in samples heat treated for 24 hours is in good agreement with the decrease of transformation enthalpy change for all heat treatment temperatures. This may be due to the fact that for the 24 hours treatment, the diffusion process may have reached equilibrium condition and therefore the distribution of atoms is more homogeneous.
Composite Deformation Behaviour

As evident in Figures 5.46 and 5.50, the apparent stress required to induce martensitic transformation increases continuously with the treatment temperature or exposure time. Similar trend of stress increase has also been observed by Liu and Galvin [17]. Recent work by Ji et al. [182] also demonstrates that the formation of oxidation-related layers on the surface of NiTi alloy causes increase of apparent stress for martensitic transformation. No explanation to this phenomenon was given in the previous studies.

This work demonstrates that the increase of stress is related to the formation of oxide-related layers and the Ti-depleted zone. It is known that the stress level for SIMT is also dependent on the equilibrium temperature of the system. All tensile deformations in this work have been carried out at a constant temperature of ~296 K. Similarly, $M_s$ temperature of the alloy remains unchanged for all heat treatment conditions, regardless of the formation of oxide and Ti-depletion, as shown in Figures 5.19 and 5.20. This implies that the increase of the stress shown here has nothing to do with the transformation temperature but purely due to mechanical resistance to deformation.

As schematically illustrated in Figure 5.55, oxidation creates “shell” layers of oxide and “dead zone” of Ti-depletion layer. These layers did not exhibit thermal martensitic transformation behaviour, thus similarly, will not exhibit stress-induced martensitic
transformation either. Therefore, the only possible mode of deformation for these layers is by dislocation slip, which follows the typical linear and nonlinear deformation behaviours. In this regard, the deformation of a sample that is comprises of “core”, “shell” and “dead zone” will be a composite deformation of two different mechanical properties, where the “core” deforms via phase transformation, meanwhile the “shell” and the “dead zone” deform via dislocation slip. Since the “shell” and “dead zone” layers do not deform via phase transformation, these layers could be considered as one entity, namely “dead layer”.

Since the “core” and the “dead layer” are always connected during the deformation, they must both have the same strain during the deformation, thus the nominal stress applied is actually divided in proportion to their area fractions. A schematic description of this deformation is illustrated in Figure 5.57.

![Figure 5.57. Schematic description of composite deformation of core and shell](image)

For this simple normal stress loading, the magnitude of nominal stress ($\sigma_o$) is equivalent to the summation of stress onto the core and the dead layer, as follows:

$$\sigma_o A_o = \sigma_{core} A_{core} + \sigma_{dead} A_{dead}$$  \hspace{1cm} (5.3)

where $\sigma_{core}$ and $\sigma_{dead}$ represent the stress on the core and on the dead layer respectively, meanwhile $A_{core}$ and $A_{dead}$ resemble the area fraction of the core and dead layer respectively. Substituting the nominal area of the sample as $A_o = A_{core} + A_{dead}$ into Equation 5.3 defines a linear relation between the increases of nominal stress with respect to the decrease of core area, as follows:

$$\sigma_o = \sigma_{core} \left( \frac{A_{core}}{A_o} \right) + \sigma_{dead} \left( 1 - \frac{A_{core}}{A_o} \right)$$  \hspace{1cm} (5.4)
In this regard, with the presence of “dead layer”, the measured nominal stress at the plateau is not the actual stress for the martensitic transformation. This stress will continue to increase as the dead layer gets thicker. This implies that the formation of dead layer from the oxide and depletion of titanium contributes to hardening effect on the stress-induced transformation. Equation 5.4 indicates that the hardening effect is possible to be estimated experimentally.

However, the accuracy of the estimation may vary depending on the real value of the $\sigma_{\text{dead}}$, and of course the thickness of the dead layer as well. On contrary, the magnitude of $\sigma_{\text{core}}$ is possible to be quantified accurately from the actual deformation behaviour of a fully recrystallised sample that has never been exposed to temperature higher than 873 K. Figure 5.58 illustrates the schematic tensile deformation behaviour of the non-SMA sample that resembles the dead layer and the NiTi-SMA that resembles the core.

![Schematic tensile deformation behaviour of the non-SMA](image)

Figure 5.58. Schematic tensile deformation behaviour of the non-SMA

It is noted that the deformation of stress-induced transformation is localised, and so the strain produced at each locality is equivalent to the magnitude of transformation strain of the stress plateau. Referring to the NiTi-SMA deformation curve above, the transformation strain ($\varepsilon_t$) is achieved at the stress level of $\sigma_{\text{core}}$, and so the global strain ($\varepsilon_o$) produced is the summation of the elastic strain ($\varepsilon_e$) of the matrix and the
transformation strain ($\varepsilon_o$). When the NiTi-SMA (core) is allowed to deform to this global ($\varepsilon_o$) strain value, the non-SMA that resembles the dead layer must also deform to the same magnitude of strain, which is also $\varepsilon_o$. Anyhow, since this region does not transform, the stress required to deform it to $\varepsilon_o$ will be $\sigma_{\text{dead}}$, following its plastic deformation curve.

This stress magnitude can vary, depending on the microstructure of the matrix. It is also dictated by the magnitude of plateau strain of the given alloy, and therefore is not necessarily limited to only yield stress. However, if it falls below the yield, it provides the chance for the core to recover the strain upon unloading. Otherwise, if the dead layer deforms beyond the plastic region, the core may be constrained from reverse transformation by the dead layer permanent deformation.

Knowing the fact that the $\sigma_{\text{dead}}$ may vary, while no complete data is available, the estimation made for calculating the apparent nominal stress at stress plateau should only be treated as an indication and not as an absolute value. Nevertheless, for the sake of equation verification, this $\sigma_{\text{dead}}$ may be considered to fall within the yield strength limit of the NiTi alloy, which is around 500-800 MPa [30]. The following parameters are taken from the sample treated at 973 K in air for 24 hours. The radius of the core is 0.71 mm and the $\sigma_{\text{core}}$ as taken from the fully recrystallised sample is 95 MPa, meanwhile the $\sigma_{\text{dead}}$ is assumed to be 500 MPa. Therefore, the calculated value of the nominal stress at the plateau based on Equation 5.2 for this sample is 141 MPa, meanwhile the measured stress as shown in Figure 5.44 is 136 MPa. This good agreement comparison provides a sensible explanation that the increase of apparent plateau stress is largely due to the hardening effect from the non-transformable “dead layer”. Similarly, the increase of transformation plateau strain as seen in Figure 5.47 is largely due to the increase of plateau stress, which provides sufficient driving force for more complete stress-induced transformation.

5.4.6 Effect of non-SMA layer on Martensite Stabilisation

As discussed above, stress-inducing this alloy may also involve plastic deformation of the shell layer. Upon unloading the external stress, strain recovery is largely depending on thickness of the “dead layer”. This is because these layers have been deformed
plastically, and so become obstruction for the core to reverse transform and recover the strain. It is noted that the stress magnitude produced by the “core” on the reverse transformation is much lower than the forward transformation. Therefore, the “dead layer” thickness will be the limit of which this reverse stress could manage to help in recovering the permanent strain of the shell. In this regard, heating the sample for reverse transformation will require much higher temperature than the martensite stabilisation effect. This is because the deformed martensite has to overcome the mechanical resistance imposed by the “dead layer” and also the martensite stabilisation effect. Unfortunately, this kind of DSC measurement has not been carried for this sample to verify this assumption. This could be proposed for future work.

5.4.7 Untransformed Austenite

In relation to the creation of “dead zone” of the Ti-depleted region from the oxidation-related process, renders to the explanation of the presence of austenite phase in stress-induced transformation martensite, as reported by Liu and Favier [142]. Their XRD analysis showed that austenite phase remained in the matrix even after the alloy had been deformed to beyond the transformation stress plateau and the testing temperature was below the $A_s$, as shown in Figure 5.59. It is found that their samples were heat treated at 1173 K in air for 30 minutes. This condition certainly caused the formation of oxide and Ti-depletion at the region near the surface, thus leading to the same effect as discussed previously. Upon loading, the core will transform into stress-induced martensite but the volume of Ti-depletion zone will remain at B2 austenite phase. Although this Ti-depleted zone contains low Ti content, it is still the B2 phase but at lower order of crystal structure and does not exhibit martensitic transformation neither via thermally-induced nor via stress-induced. This is proven in Figure 5.59(b), where the sample was reheated at 423 K (temperature above $A_f$), but still detected with B2 phase. It is seen also that the B2 phase begin to reduce when the alloy was deformed to 26% of the global strain. This reduction however only indicates the lost of B2 crystal structure due to severe distortion and slip of the atoms.
Figure 5.59. X-ray diffraction spectra of Ti-50.15at%Ni: (a) after deformation at 298 K and (b) after reheated to above $A_s$ temperature [142]
FUNCTIONALLY GRADED Ni-Ti

6.1 Thermal and Mechanical Transformation Behaviour of Conventional Polycrystalline NiTi

Ni-Ti shape memory alloys are known to be among the best candidates for many engineering applications, in particular, as sensors, actuators and fixtures. Examples of applications in actuation and control include flow-restricting thermostats, refrigerant expansion valves, safety valves for cooling of internal combustion engines and flow control valves [30, 183]. Ni-Ti alloys perform these actions via its thermoelastic martensitic transformation, induced by either temperature variations or the application of stress. Such material transformation-based actuation mechanism allows design of very simple structures, devices and apparatuses without complex mechanical design, thus subsequently reduces the cost of manufacturing, assembly and maintenance.

In some of these designs the shape memory apparatus is required to take a sudden action when the external stimulus reaches a threshold value, whilst in some other designs the shape memory apparatus requires controlled action over a certain range of the control parameter, typically temperature or stress.

However, the thermoelastic martensitic transformation in NiTi has intrinsically small transformation temperature intervals, typically <10 K [169, 184], with the bulk of the transformation occurring within a narrower range of ~5 K, as shown in Figure 6.1(a). The stress interval of a stress-induced transformation is fundamentally determined by the thermal interval and is usually also very small.
Tensile stress-strain behaviour of slender polycrystalline NiTi via stress-induced transformations, in either the shape memory effect or the pseudelasticity, generally exhibits a typical localised deformation phenomenon, as shown in Figure 6.1(b). Such behaviour is referred to in the literature as the Lüders-type deformation [130-132, 185]. Similar deformation behaviour is also observed for deformation of martensite via variant reorientation [132]. The Lüders-type deformation is characterised by two stress plateaus associated with the forward and the reverse martensitic transformations [131, 186].

In this case the transformation occurs over a single value of stress, i.e. with a zero stress interval. When such critical stress is reached, the alloy deforms to full completion of the transformation in one rapid jump, leaving no option for any progressive or intermediate state of displacement. This imposes difficulties in controlling the motion of a shape memory apparatus, or the process of the transformation, by controlling precisely small variations of the external input signals of temperature or stress. This severely reduces the controllability of the alloys and limits the versatility and applicability of many shape memory devices.

To overcome this problem, it is necessary to expand the windows of these control parameters. A possible approach to improving these limitations is to create functionally graded NiTi materials in which the martensitic transformation may occur at a different temperature or stress at different locations along their lengths. By having this, the
martensitic transformation is allowed to occur within wide temperature and stress ranges, reducing the sensitivity requirement for control and improving the controllability of the devices. One way to achieve this is by altering its microstructure via heat treatment. It is known that properties of near-equiatomic Ni-Ti are very sensitive to heat treatment conditions (microstructure), including both annealing after cold working and ageing after solution treatment. It has been reported in the literature that the forward transformation temperature of near-equiatomic NiTi alloys decreases drastically with lowering the annealing temperature whereas the reverse transformation temperature shows a moderate increase [35, 147]. Accompanying the decrease of the forward transformation temperature, the critical stress to induce the transformation at a given temperature increases [17, 36, 187], as predicted by the Clausius-Clapeyron relation [44, 45, 188]. Similarly, ageing process also changes the transformation behaviour by the formation of coherent precipitates, most notably Ti3Ni4. By controlling the process of artificial ageing (i.e., the size, morphology, amount and the type of the precipitates), properties of NiTi can be adjusted and tailored within a wide range.

Based on these concepts, this work aims to design a novel heat treatment process to produce NiTi materials with gradient microstructures, hence gradient shape memory properties. The design focused on the effect of annealing and ageing temperature on the transformation temperature and the critical stress for stress-induced transformation of near-equiatomic NiTi alloys. The alloys used for the annealing effect was Ti-50.5at%Ni and that for the ageing effect was Ti-50.8at%Ni. Both of them are in the form of wires with diameters of 1.5 mm and 0.7 mm, respectively.

To enable the design of functionally graded NiTi and the heat treatment conditions for gradient annealing and gradient ageing, a comprehensive database on thermal and mechanical behaviour of isothermally annealed and aged samples is necessary. This provides the ranges and limits of the temperature for gradient annealing and temperature-time for gradient ageing. Subsequently, the potentially achievable functionally gradient thermomechanical behaviour of the alloy can be predicted.
6.2 Gradient Temperature Annealing

6.2.1 Thermal Transformation Behaviour of Isothermally Annealed NiTi

Figure 6.2 shows the thermal transformation behaviour of Ti-50.5at%Ni alloy from the isothermally annealed samples. The transformation behaviour of this alloy is similar to those shown in Figure 4.1 in Chapter 4. The cold work percentage done on these samples was 50% by elongation. It is evident from this figure that at 848 K the sample has been fully recrystallised. Knowing that the percentage of prior cold work before annealing affects the transformation behaviour (as discussed in Chapter 4), therefore it is more appropriate to differentiate their transformation behaviours, thus a more accurate measurement on transformation temperature is achieved. Similar practice will also be done on deformation behaviour of the alloy, in the following section.

![Figure 6.2. Thermal transformation behaviour of Ti-50.5at%Ni after isothermally annealed at different temperatures for one hour](image-url)
6.2.2 Deformation Behaviour of Isothermally Annealed NiTi

Figure 6.3 shows the deformation behaviour of the Ti-50.5at%Ni alloy as determined from the isothermal samples. The samples were deformed in tension at 313 K. Samples annealed at above 773 K showed no pseudoelasticity at this testing temperature. As the annealing temperature lowered, the critical stress to induce the transformation increased progressively and the transformation strain decreased. Wires annealed at 723 K and 673 K showed the R-phase transformation at the early stage of deformation, as seen in the small shoulder of less than 1% strain at below 100 MPa. Pseudoelasticity was achieved in samples annealed at 723 K and below at this testing temperature. It is also to be noted that the stress hysteresis of the pseudoelasticity decreased with lowering the anneal temperature.

![Stress vs Strain Graph for Ti-50.5at%Ni](image)

Figure 6.3. Tensile deformation behaviour of Ti-50.5at%Ni isothermally annealed at different temperatures and tested at 313 K

Figure 6.4 shows the effect of annealing temperature on the critical stress and transformation strain for samples deformed at 313 K, as deduced from Figure 6.3. It is seen in (a) that the critical stress for the forward transformation, $\sigma_{fwd}$, decreased linearly as the annealing temperature increased. However, the critical stress for the reverse
transformation, $\sigma_{\text{rev}}$, decreased more drastically when the annealing temperature increased to above 623 K. This caused the stress hysteresis, $\sigma_{\text{hyst}}$, to increase following the increase of annealing temperature. Figure 6.3(b) shows that both transformation strains of the forward ($\varepsilon_{fwd}$) and the reverse ($\varepsilon_{\text{rev}}$) transformations increased as the annealing temperature increased. Both curves appear to approach a maximum transformation strain of 7.5% in fully recrystallised samples annealed at above 823 K, at the testing temperature of 313 K. The reverse transformation strain was always smaller than the forward transformation strain.

![Graph](image1)

Figure 6.4. Effect of annealing temperature on the (a) critical stresses for inducing the transformations and (b) transformation plateau strains

Figure 6.5 shows the effect of annealing temperature on the yield strength and the critical stress for the forward stress-induced martensitic transformation of the alloy, tested at two different temperatures (313 K and 295 K). A fresh sample was used for each testing to avoid the effect of cycling [17]. The yield strengths were measured from the samples deformed at 295 K. It is evident that both the yield strength and the critical stress for inducing the martensitic transformation (at a given temperature) decreased with increasing the anneal temperature. For the purpose of creating a functionally graded NiTi, it is necessary to ensure that the yield strength at the weakest end (the lowest yield strength) must be greater than the highest critical stress for inducing the transformation. Otherwise, the weak end (high anneal temperature) of the material will experience plastic deformation prior to the occurrence of stress-induced transformation at the stronger end. In this regard, the effective annealing temperatures for functional graded NiTi fall within the shaded area (as for the particular case of testing at 313 K).
Figure 6.5. Effect of annealing temperature on yield strength and critical stresses for inducing martensitic transformation at different temperatures

For example, a wire sample may be heat treated within a temperature range between T1 and T2, as indicated by heat treatment line HT1. Under this condition, the specimen is expected to commence the stress-induced martensitic transformation upon loading at 313 K at $\sigma_1$ from the end that had been annealed at T1 and to complete the transformation at $\sigma_2$ at the end that had been annealed at T2. As another option, a wire sample may be annealed within the temperature range of T3-T4, as indicated by heat treatment line HT2. In this case, the stress-induced martensitic transformation may start at $\sigma_3$ and reach completion at $\sigma_4$. Clearly, HT2 is the lowest effective temperature range for the gradient anneal. However, with respect to a different expected application temperature, for example 295 K, the heat treatment design may be different. For instance, in this case the HT1 line may extend to be between T1-T5, and the expected stress range for the stress-induced martensitic transformation is $\sigma_6$-$\sigma_5$. This is practically the largest temperature window (873 K – 595 K) for the gradient anneal and the largest stress interval (80 MPa - 430 MPa) for the forward stress-induced martensitic transformation for the Ti-50.5at%Ni alloy. It is obvious that the effective temperature window for gradient anneal is defined by the gap between $\sigma_y$ and $\sigma_{fwd}$, and narrows with increasing deformation temperature. It is also worth noting that, in the middle sections where the $\sigma_y$ and $\sigma_{fwd}$ curves appear reasonably linear, their dependencies on annealing
temperature may be estimated to be approximately -2.5 MPa/K for $\sigma_{y}$, -1.7 MPa/K for $\sigma_{fwd}$ at 313 K, and -1.6 MPa/K for $\sigma_{fwd}$ at 295 K. These parameters are useful as empirical data for designing the heat treatment conditions.

Regarding the $\sigma_{fwd}$ curves as linear functions of the anneal temperature (for simplicity in discussion), the stress-strain behaviour of the gradient-annealed samples may be predicted as schematically shown in Figure 6.6, as for the case of deformation at 313 K. Curve (1) represents the deformation behaviour of the sample annealed according to HT1 and curve (2) represents the deformation behaviour of the sample annealed according to HT2. Curve (3) represents an arbitrary sample annealed according to any heat treatment condition between HT1 and HT2. The stress gradient for the stress-induced martensitic transformation for samples (1) and (2) are 3.3 GPa and 4.7 GPa, respectively. It is clear that by selecting different gradient anneal temperature profiles it is possible to tailor the level of stresses required at a particular application temperature.

![Figure 6.6](image)

**Figure 6.6.** Schematic illustration for deformation behaviour of gradient-annealed Ti-50.5at%Ni at 313 K

The gradient anneal was conducted using a tube furnace. The furnace was purposely controlled to produce a temperature gradient within its hearth. Figure 6.7 shows the temperature distribution profile along the hearth of the furnace. The preset maximum temperature for the furnace for this particular treatment was 823 K. The temperature distribution was nonlinear. The temperature range selected for a heat treatment was 630
K – 810 K, defining a spatial length of 100 mm. This corresponds closely to the HT2 condition shown in Figure 6.4. NiTi wires of 120 mm in length were placed inside the furnaces, with 10 mm of its length extending out of the extremities of the temperature range in each end (for gripping for deformation testing), as schematically shown in the figure.

![Temperature distribution profile of the furnace hearth used for the gradient anneal](image)

**Figure 6.7.** Temperature distribution profile of the furnace hearth used for the gradient anneal

### 6.2.3 Thermal Transformation Behaviour of Gradient-Annealed NiTi

Figure 6.8 shows DSC measurements of thermal transformation behaviour of six specimens taken at different positions along the length of the gradient annealed wire sample. The specimen positions were referred from the low temperature end of the wire. For example, specimen (a) was taken at the high temperature end of the wire, which was 100 mm from the low temperature end of the wire. Similarly, specimen (b) was taken at 80 mm and specimen (f) was taken at 5 mm from the low temperature end of the wire. According to Figure 6.7, the corresponding annealing temperature for each specimen is shown in the bracket. It is evident that these specimens exhibited progressively varying transformation behaviour, demonstrating the graded property. The transformation behaviour of each of these specimens is very similar to that of their respective isothermally annealed samples shown in Figure 6.2.
Figure 6.8. Thermal transformation behaviour of gradient-annealed Ti-50.2at%Ni samples

Specimens (a), (b) and (c) exhibited well-defined two-stage transformation sequence of $\text{B2} \rightarrow \text{R} \rightarrow \text{B19'}$ on cooling and a single-stage $\text{B19'} \rightarrow \text{B2}$ transformation on heating. Specimens (d), (e) and (f), which were annealed at lower temperatures, exhibited much broadened transformation peaks. The cooling transformation is still in two stages, with the $\text{R} \rightarrow \text{B19'}$ transformation appearing at much lower temperatures and the $\text{B2} \rightarrow \text{R}$ transformation at higher temperatures, as compared to specimens (a), (b) and (c). On heating, the specimens exhibited two-stage transformations of $\text{B19'} \rightarrow \text{R} \rightarrow \text{B2}$.

Figure 6.9 shows the peak temperatures of the transformations of specimens taken from the gradient-annealed wire (open symbols). Transformation temperatures of the isothermally annealed samples (closed symbols) are also included for comparison. The x-axis on top of the frame indicates the position of the gradient-annealed DSC specimen for each measurement. The x-axis below is the corresponding annealing temperatures of the specimens as converted from their positions according to the graph shown in Figure 6.7. Therefore, this figure expresses the effect of annealing temperature on the transformation temperatures. It is seen that the corresponding transformation
temperatures from the gradient-annealed specimens match closely with the isothermal samples. This implies that a gradient temperature annealing is successfully done along the length of the 100 mm specimen.

For this alloy system, it is seen that the annealing temperature range may be divided into three regions. In Region I, \( T^{AR} \) for the B2→R transformation increased while \( T^{RM} \) for the R→B19' transformation decreased continuously rather linearly with decreasing annealing temperature. In Region II below 650 K, \( T^{AR} \) and \( T^{RM} \) showed little dependences on annealing temperature. The R→B19' transformation was too broad to allow accurate determination of its critical temperature. The data shown in the figure for \( T^{RM} \) in Region II are only indicative. The temperature of the reverse transformation of R→B2 (\( T^{RA} \)) followed the same trend as \( T^{AR} \). In Region III above 840 K, \( T^{AM} \) and \( T^{MA} \) remained constant values and independent of annealing temperature. This corresponds to the fully annealed state. Obviously Region I is the effective annealing temperature range for gradient anneal.
6.2.4 Deformation Behaviour of Gradient-Annealed NiTi

Figure 6.10 shows the deformation behaviour of two gradient-annealed wire samples in tension at 313 K. Sample (a) was at the full length of 100 mm, where the temperature gradient of the annealing, as interpolated from the furnace profile (Figure 6.7), was 630-810 K. Sample (b) represents the temperature gradient of 630-783 K after 30 mm of its length was removed from the high temperature end of the wire. The samples were initially heated to above 330 K prior to cooling down to 313 K for the testing. The testing temperature is indicated in Figure 6.9 by the dashed horizontal line. It is seen that the part of the sample annealed at low temperatures were in the R-phase state and that at high temperature were austenite.

Deformation of the samples showed a unique Lüders-type behaviour with a progressively increasing stress. The start of the “gradient stress plateau” corresponds to the localised stress-induced martensitic transformation at the end of the wire sample that had been annealed at the highest temperature, and the finish of the “gradient stress plateau” represents the other end of the wire with the lowest anneal temperature. Sample (a) showed a lower positive stress gradient as compared to sample (b) in the early deformation. This is attributed to a relatively greater length proportion of high anneal temperature (783 - 810 K) at the end of the wire, which was due to the nonlinear
furnace temperature profile, as seen in Figure 6.7. In this regard, sample (b) is considered a better option for achieving a linear gradient stress plateau. In addition, it is also apparent that sample (b) showed a more pronounced deformation of ~0.2% by the R-phase. This is clearly related due to the fact that most of the length of sample (b) started with an R-phase structure.

The Lüders-type deformation of sample (b) yielded a transformation strain of ~7.5% and extended over a stress interval of ~270 MPa from 280 to 550 MPa. The estimated stress gradient for the stress-induced forward transformation is 4.7 GPa. Considering that the range of the annealing temperature for sample (b) was $\Delta T_{\text{anl}} = 153$ K and that the stress interval for the stress-induced martensitic transformation was $\Delta \sigma_{\text{SIM}} = 275$ MPa, it can be estimated that the effect of gradient annealing temperature on the “gradient stress plateau” is approximately:

$$\eta = \frac{\Delta \sigma}{\Delta T} = 1.76 \text{MPa} / K$$

(6.1)

This value agrees well with the anneal temperature dependences estimated based on the testing of the isothermal samples shown in Figure 6.5.

It is also seen that the sample exhibited incomplete pseudoelasticity. The (total) recovered strain upon unloading is 5%, corresponding to ~60% of the total deformation. The pseudoelastic reverse transformation showed a much steeper slope of its “gradient stress” compared to that of the forward transformation, at ~8.6 GPa. This gives rise to an unequal stress hysteresis for the pseudoelastic “loop”, with the stress hysteresis being smaller at the high deformation end and large at the low deformation end. This is consistent with the observation shown in Figure 6.4, that the pseudoelastic stress hysteresis decreases with decreasing anneal temperature. This phenomenon can also be logically illustrated based on the stress hysteresis produced from the isothermal-annealed samples as shown in Figure 6.11. This figure shows the effect of annealing temperature on the critical stresses for the forward and the reverse transformations of the samples deformed at 313 K (as from Figure 6.4).

The anneal temperature is plotted on the x-axis in the reverse direction for easy direct comparison with the stress-strain curve shown in Figure 6.10. It is seen that the two
critical stresses increased with decreasing annealing temperature and that the stress hysteresis decreased. The anneal temperature dependences of $\sigma_{\text{fwd}}$ and $\sigma_{\text{rev}}$ are estimated to be approximately -1.7 MPa/K and -3.0 MPa/K, respectively. Comparing with Figure 6.10, it is clear that the two figures resemble a similar shape implying that the stress-strain curve at the high strain end of the pseudoelastic loop represents the deformation of the part of the wire sample that had been annealed at the lowest temperatures and that the part of the stress-strain curve at the low strain end represents the deformation of the part of the wire sample that had been annealed at the higher temperatures. The observed partial pseudoelasticity in Figure 6.10 is also explained clearly in Figure 6.11, where $\sigma_{\text{rev}}$ decreased to zero when the anneal temperature increased to above 723 K.

![Graph showing critical stresses for the forward and reverse transformations of Ti-50.5at%Ni as deformed in tension at 313 K of samples isothermally annealed at different temperatures](image)

**Figure 6.11.** Critical stresses for the forward and reverse transformations of Ti-50.5at%Ni as deformed in tension at 313 K of samples isothermally annealed at different temperatures

### 6.2.5 Variable Plateau Stress Gradient

Figure 6.12 and 6.13 show the deformation behaviour of gradient-annealed samples from different gage lengths, demonstrating effects of different temperature ranges of the annealing. The length of the samples shown in Figure 6.12 was measured from the high temperature end of the wire, and for Figure 6.13 the length was measured from the low temperature end. The wires were deformed in tension at 313 K. The corresponding annealing temperature range for each length of the wire is tabulated in Table 6.1.
As seen in Figure 6.12, the slope of the plateau stress increased progressively as the length of the wire increased. In all cases, the start of the forward stress-induced transformation, \( \sigma_{\text{start}}^{\text{fwd}} \), happened at a similar stress level of \( \sim 280 \text{ MPa} \), which is obviously related to the high temperature end of the wire (810 K). The end of the gradient stress, \( \sigma_{\text{end}}^{\text{fwd}} \), represents the corresponding low temperature end of the wire. On the other hand, the transformation plateau strain decreased as the length increased. This corresponds well with the decreased of transformation strain as the annealing temperature decreased, as shown in Figure 6.4. Similarly, the recovery strain achieved on the reverse transformation improved as the length increased.

Figure 6.12. Tensile deformation behaviour of gradient-annealed Ti-50.5at\%Ni at 313 K, with different lengths as taken from the high temperature end

Figure 6.13 shows the deformation behaviour of samples of various lengths cut from the low temperature end. It is seen that the plateau for all specimens ended at the same stress of \( \sigma_{\text{end}}^{\text{fwd}} \sim 540 \text{MPa} \), and the start of the stress plateau, \( \sigma_{\text{start}}^{\text{fwd}} \), decreased as the length of the wire increased. The two shortest samples (10 mm and 20 mm) showed reasonably good pseudoelasticity, with \( \sim 4\% \) recovery strain, but at very low slope of stress gradient. Also, it is worth to mention that the early stage of deformation of these specimens showed the presence of R-phase transformation, as seen in the small shoulder.
of less than 1% strain at below 100 MPa. However, this was not observed in Figure 6.12. This implies that the presence of R-phase stress-induced transformation is associated with the low annealing temperature portion of the wire.

![Graph showing tensile deformation behaviour of gradient-annealed Ti-50.5at%Ni at 313 K, with different lengths as taken from the low temperature end.]

Figure 6.13. Tensile deformation behaviour of gradient-annealed Ti-50.5at%Ni at 313 K, with different lengths as taken from the low temperature end.

<table>
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<th>Wire Length (mm)</th>
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<th>Wire Length (mm)</th>
<th>Temperature Range (K)</th>
<th>Measured from low temperature end (Figure 6.13)</th>
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<td>630 – 713</td>
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<td>758 – 810</td>
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<td>630 – 743</td>
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6.2.6 Effect of Testing Temperature on Deformation Behaviour of Gradient-Annealed NiTi

Figure 6.14 shows the deformation behaviour of the gradient-annealed samples at few testing temperatures. A new sample was used for each test to avoid the effect of deformation cycles. Deformation at 303 K showed a clear presence of R-phase transformation at the early stage of deformation, with ~0.6% strain at below 50 MPa. The level of plateau stress increased and the transformation recovery strain improved as the testing temperature increased. Good pseudelasticity was achieved from samples deformed at 323 K and 333 K. The linearity of plateau stress slope seems to deteriorate as the testing temperature increased. This effect is more obvious at the low annealing temperature section (lower side of plateau stress level).

![Figure 6.14. Tensile deformation behaviour of gradient-annealed Ti-50.5at%Ni at different temperatures](image)

Figure 6.15 shows the effect of testing temperature on the forward transformation stress of the gradient-annealed samples. $\sigma_{\text{start}}^{\text{fwd}}$ was taken at the start of the gradient stress plateau, as shown in Figure 6.14, and $\sigma_{\text{end}}^{\text{fwd}}$ was taken at the end of the plateau. It is evident that the increase of critical stress for stress-induced martensitic transformation with respect to testing temperature follows the linear Clausius-Clapeyron relation [8],

\[ \Delta H = \frac{\Delta S}{T} \]
and their values agree well with the published data [35, 147, 177]. However, it is seen that the rate of increase of $\sigma_{\text{fwd, start}}$ is higher than that of $\sigma_{\text{fwd, end}}$. This implies that the low annealing temperature end of the wire experienced lesser effect from test temperature. The $\sigma_{\text{fwd, interval}}$ line represents the stress interval of the forward transformation stress plateau. Due to the lower slope of $\sigma_{\text{fwd, end}}$, the stress interval decreased as the testing temperature increased. This suggests that a maximum stress interval is achievable at low testing temperatures.

![Figure 6.15. Temperature-dependent of stress-induced transformation](image)

**6.2.7 Deformation Cycle of Gradient-Annealed NiTi**

Figure 6.16 shows the deformation cycle of gradient-annealed sample at 333 K. It is seen that the sample managed to exhibit good pseudoelastic behaviour after cycling. The unrecovered strain upon completion of reverse transformation on the first cycle was ~0.75%. The recovery rate of strain improved as the number of cycles increased. The stress level of plateau stress gradient decreased marginally after the first cycle but began to stabilize after 5 cycles. The slope of the plateau stress gradient remained at nearly constant value with further cycling. The partial cycle in the last deformation cycle provides clear evidence that at any particular stress level, a stress-induced martensitic transformation only occurred at a localised region of the wire, which corresponds to its unique microstructure condition, as a result of the annealing temperature. Alternatively,
the nucleation of stress-induced martensite will always start at the high temperature end of the wire and its growth towards the low temperature end of the wire is delayed by the speed of the incremental external load applied. In this regards, the rapid jump of full transformation is avoided and a better control for progressive displacement is feasible.

Figure 6.16. Cyclic deformation of gradient-annealed Ti-50.5at%Ni at 333 K

6.3 Gradient Temperature Ageing

Unlike partial anneal, the effects of ageing on thermal and mechanical behaviour of NiTi alloys are far more complicated. As elaborated in Chapter 2, effect of ageing is dependent on three independent parameters: alloy composition, ageing time and ageing temperature. Ageing at temperatures below 600 K for short time suppresses the original $B2 \rightarrow B19'$ transformation [121]. On the other hand, ageing at higher temperatures above 600 K for long time may cause “multi-stage” transformation behaviour [108, 119, 121, 151]. These complicate the prediction of stress level for inducing martensitic transformation.

Design for gradient ageing treatment must integrate both the ageing time and temperature parameters at their optimum effects. On the other hand, varying the alloy composition may also affect the ageing time and temperature significantly. In this regard, it is a great challenge for developing an effective gradient ageing process for
achieving a good gradient mechanical behaviour for Ni-rich NiTi alloys. The focus of this study is to gather a comprehensive data on the effect of ageing time and temperature towards martensitic transformation deformation behaviour of Ti-50.8at%Ni. This study will serve as a preliminary approach to designing the gradient ageing process from two possibilities: (a) gradient temperature ageing and (b) gradient time ageing.

6.3.1 Thermal Transformation Behaviour of Isothermally Aged NiTi

Figure 6.17 shows the thermal transformation behaviour of Ti-50.8at%Ni after isothermal ageing at 573 K for different times. The transformation behaviour of a solution treated sample is also included for reference. It is well known that the transformation behaviour of Ni-rich alloys after ageing treatment may exhibit “multi-stage” transformations [108, 119, 121, 150, 151]. This phenomenon has been well explained based on the effects of long-range heterogeneity of precipitate structure between grain boundaries and grain interior and short-range heterogeneity caused by over-growth of coherent precipitates into the formation of incoherent precipitates [121].

The solution treated sample exhibited a single stage transformation of $A_0 \leftrightarrow M_0$, with the forward peak temperature of $A_0 \rightarrow M_0$ happened at 265 K and the reverse peak temperature of $M_0 \rightarrow A_0$ occurred at 291 K. Sample aged for 30 minutes showed minimum effect of ageing towards transformation temperature change. Samples aged for 1 hour and longer showed the presence of R-phase transformation and suppression of the original $B2 \rightarrow B19'$ ($A_0 \leftrightarrow M_0$) on cooling. In this case, the austenite phase is labelled as $A_1$ and the R-phase is labelled as $R_1$. Occurrence of the $A_1 \leftrightarrow R_1$ transformation can be verified via partial cycle measurements, as inserted in the DSC measurement of samples aged for 1 hour and 2 hours, as in Figure 6.7. Transformation of $R_1 \rightarrow A_1$ on the full cooling-heating cycle was not observed in samples aged for 1 hour and 2 hours because it was thermodynamically prohibited. Therefore, the transformation on the heating showed only a single stage of $M_1 \rightarrow A_1$. As the ageing prolonged, the $A_1 \rightarrow R_1$ temperature on cooling increased continuously and the $M_1 \rightarrow R_1$ transformation on heating began to appear in samples aged for 4 hours and longer. The $A_1 \leftrightarrow R_1$ transformation peak became narrower as the ageing time increased, but the $R_1 \leftrightarrow M_1$ transformation peak became broader.
Figure 6.17. Transformation behaviours of Ti-50.8at%Ni aged at 573 K

Figure 6.18 shows the thermal transformation behaviour of Ti-50.8at%Ni after isothermal ageing at 623 K for different times. Samples aged for 2 hours and shorter showed a single stage transformation of $A_0 \leftrightarrow M_0$. The $A_1 \leftrightarrow R_1$ transformation only began to appear after 4 hours of ageing. All samples aged for 4 hours and longer exhibited a single transformation of $M_1 \leftrightarrow A_1$ on heating. It is also noted that the $A_0 \leftrightarrow M_0$ transformation occurred with a very small peak in sample aged for 4 hours with its reverse transformation expected to occur within the temperature window of $M_1 \leftrightarrow A_1$ transformation. This transformation disappeared after 8 hours of ageing.
Figure 6.18. Transformation behaviours of Ti-50.8at%Ni aged at 623 K

Figure 6.19 shows the thermal transformation behaviour of Ti-50.8at%Ni after isothermal ageing at 673 K for different times. As similar with Figure 6.18, a single stage transformation of $A_0 \leftrightarrow M_0$ was observed from samples aged for 2 hours and shorter. Ageing for 4 hours resulted in four stages of transformation, including $A_1 \rightarrow R_1 \rightarrow M_1$, $A_0 \rightarrow M_0$ and $A_2 \rightarrow M_2$. The occurrence of $A_2 \rightarrow M_2$ is verified in Figure 6.20. A partial heating measurement showed that the $A_2 \rightarrow M_2$ peak on cooling, immediately before the $A_0 \rightarrow M_0$ peak was not observed. Subsequent heating beyond the $M_2 \rightarrow A_2$ peak caused the $A_2 \rightarrow M_2$ peak to reappear, demonstrating the correlation between $M_2 \rightarrow A_2$ and $A_2 \rightarrow M_2$. The $A_2 \rightarrow M_2$ transformation is attributed to the austenite phase from the Ni-depleted region. This region is expected to be near the Ni-rich incoherent precipitates in the matrix.

Transformation on the heating for sample aged for 4 hours only involved two-stage transformations of $M_0 \rightarrow A_0$ and $M_2 \rightarrow A_2$. The $M_1 \rightarrow R_1 \rightarrow A_1$ transformation was not observed due to the fact that the volume percentage of this phase in this sample was too
small, thus the transformation may have not been detected. This phenomenon can be further verified from the sample aged for 8 hours where a weak peak of \( R_1 \leftrightarrow A_1 \) reappeared at \(~320\) K. It is also observed that the size of the \( A_0 \leftrightarrow M_0 \) peak decreased significantly as the ageing time increased and its reverse transformation disappeared within the \( M_1 \leftrightarrow R_1 \) transformation temperature window. On the other hand, the \( A_2 \leftrightarrow M_2 \) peak size increased as the ageing time increased, signifying that the volume percentage of Ni-depleted region increased proportionally, at the consumption of the original \( A_0 \) phase. It is also found that the \( A_2 \leftrightarrow M_2 \) temperature increased continuously as the ageing temperature increased, while the temperature interval remained at around 40-45 K. This suggests that the depletion of Ni in the region near the precipitates decreased the Ni content in the alloy continuously as the ageing temperature increased.

![Figure 6.19. Transformation behaviours of Ti-50.8at%Ni aged at 673 K](image-url)
Figure 6.20. Partial transformation cycle of sample aged at 673 K for 4 hours

Figure 6.21 shows the thermal transformation behaviour of Ti-50.8at%Ni after isothermal ageing at 723 K for different times. The transformation behaviour observed in this figure is similar to the transformation behaviour shown in Figure 6.19, except that the effect of ageing at this temperature was more aggressive where the multistage transformation occurred at much earlier ageing time (after 1 hour), as compared to ageing at 673 K. Sample aged for 1 hour and longer exhibited three peaks of transformation on heating. The first peak seems to be a mixture of $M_0 \rightarrow A_0$ and a small fraction of $M_1 \rightarrow R_1$, suggested by the small size of the $R_1 \rightarrow A_1$ peak. Samples aged for 8 hours and longer showed the separation of $M_0 \rightarrow A_0$ and $M_i \rightarrow A_1$, after the $M_1 \rightarrow R_1 \rightarrow A_1$ transformation was thermodynamically prohibited. This phenomenon is further verified in Figure 6.22 from the sample aged for 24 hours. Partial cooling of the sample showed that the $R_1 \rightarrow M_1$ and $A_2 \rightarrow M_2$ transformations may have occurred within wide temperature window and the $R_1 \rightarrow A_1$ can be allowed to occur if the heating is done before the start of $R_1 \rightarrow M_1$ transformation on cooling. It is also observed that the temperature interval of $A_2 \leftrightarrow M_2$ decreased continuously as the ageing temperature decreased. This suggests the phase may have approached its equilibrium stability upon the growth of homogeneous precipitates in the matrix.
Figure 6.21. Transformation behaviours of Ti-50.8at%Ni aged at 723 K

Figure 6.22. Partial cycles of sample aged at 723 K for 24 hours
Figure 6.23 shows the thermal transformation behaviour of Ti-50.8at%Ni after isothermal ageing at 773 K for different times. The transformation behaviour is similar to those shown in Figures 6.19 and 6.21. These results demonstrate that the effect of ageing becomes more aggressive as the ageing temperature increases.

![Diagram](image)

**Figure 6.23. Transformation behaviours of Ti-50.8at%Ni aged at 773 K**

Figures 6.24 and 6.25 show the effect of ageing time on transformation peak temperatures of samples aged at 573 K and 723 K, respectively. The effect of ageing time on samples aged at 623 K is not shown here because the pattern of the transformation sequences and changes were similar to the samples aged at 573 K. Similarly, the samples aged at 673 K and 773 K are not included because the effects were similar to the samples aged at 723 K. The $A \leftrightarrow M$ peak temperatures of the solution treated sample is marked with “soln” in the figures.

For the samples aged at 573 K (Figure 6.24), the original martensitic transformation $B2 \leftrightarrow B19^\prime$ ($A_0 \leftrightarrow M_0$) existed over a very short period of time and its temperature...
remained little changed. With ageing \(R_1 \rightarrow M_1\) emerged and its temperature remained practically constant with ageing time. The \(A_1 \rightarrow R_1\) emerged at above the original \(A_0 \rightarrow M_0\) and its temperature increased moderately with ageing time. The \(R_1 \rightarrow A_1\) transformation followed the same trend as \(A_1 \rightarrow R_1\). The \(M_1 \leftrightarrow R_1\) transformation emerged from very low temperature and increased rapidly as the ageing time increased, and began to stabilise after 8 hours. Figure 6.25 shows that the increases of \(A_1 \leftrightarrow R_1\) temperatures were mild as the ageing time increased reaching a steady state after 8 hours of ageing.

Figure 6.24. Effect of ageing time on transformation temperatures; ageing at 573 K

The samples aged at 723 K (Figure 6.25) always exhibited the \(A_0 \leftrightarrow M_0\) transformation, and its temperatures remained little changed for all ageing times, except a small increase in the first hour of ageing. This is believed to be an artefact due to the overlap of other emerging transformations. Temperatures of other transformations, including \(R_1 \rightarrow M_1\), \(A_1 \leftrightarrow R_1\) and \(A_2 \leftrightarrow M_2\) all increased with increasing ageing time.
Figure 6.25. Effect of ageing time on transformation temperatures; ageing at 723 K

Figure 6.26 demonstrates the effect of ageing from the temperature perspective towards transformation peak temperatures of samples aged for 2 hours. The effect of ageing temperature from samples aged for the other hours are not shown here because the pattern of the transformation sequences and changes were near similar. It is seen that $A_0 \leftrightarrow M_0$ temperatures remained constant for all ageing temperature. On the other hand, the $R_1 \rightarrow M_1$ forward transformation temperature decreased as the ageing temperature decreased. The $A_1 \rightarrow R_1$ showed a mild increase of temperature as the ageing temperature decreased but continued to decrease as the ageing temperature dropped to below 723 K.
6.3.2 Deformation Behaviour of Isothermally Aged NiTi

Figure 6.27 shows the deformation behaviour of Ti-50.8at%Ni after isothermal ageing at 573 K for different times. The samples were deformed in tension at 295 K. The forward stress-induced $\text{B}_2 \rightarrow \text{B}_{19}'$ martensitic transformation of the solution treated sample occurred at $\sim 400 \text{ MPa}$, with nearly $10\%$ plateau strain. Samples aged for 30 and 15 min showed good linear elastic deformation in the early stage of deformation but began to deform nonlinearly at $\sim 250 \text{ MPa}$, signifying the start of the uniform stage of stress-induced $\text{B}_2 \rightarrow \text{B}_{19}'$ martensitic transformation, prior to the onset of the stress plateau, which represents the localisation of the stress-induced martensitic transformation. The sample aged for 1 hour preceded by stress-induced $\text{B}_2 \rightarrow \text{R}$, as evident by the small non-linear shoulder of stress at $\sim 200 \text{ MPa}$ prior to the onset of the stress plateau. Samples aged for 2 hours and longer showed stress-induced R-phase reorientation at the early stage of deformation. As evident in Figure 6.17, these samples were in the R-phase prior to the deformation. In these regards, the transformation plateau obtained from samples aged for 1 hour and longer was associated with the stress-induced $\text{R} \rightarrow \text{B}_{19}'$ transformation. It is seen that he critical stress for inducing the
martensitic transformation decreased marginally but the plateau strain decreased significantly as the ageing time increased.

Good pseudoelasticity, although not complete, was achieved from all samples, except the one aged for 24 hours and the solution treated sample. The sample aged for 24 hours showed a significant drop of the stress for inducing the martensitic transformation. This sample has obviously been over aged.

![Figure 6.27: Tensile deformation of Ti-50.8at%Ni after isothermally aged at 573 K](image)

Figure 6.28 shows the deformation behaviour of samples aged at 623 K. Samples aged for 2 hours and shorter exhibited stress-induced B2\(\rightarrow\)R transformation at above ~125 MPa, thus the transformation plateau implied the R\(\rightarrow\)B19’ transformation. Samples aged for 4 hours and longer were preceded by the R-phase reorientation. Pseudoelasticity was achieved from samples aged for up to 2 hours. This implies that over ageing may have happened after 4 hours of heating at 623 K. Additionally, the testing temperature was far lower than the reverse transformation temperature of these samples (Figure 6.18).
It is noted that the stress level of the sample aged for 8 hours was higher than the sample aged for 4 hours. This could be attributed to the fact that the stress-induced transformation of sample aged for 4 hours was a mixture of two separate martensitic transformations. Referring to Figure 6.18, the transformation temperatures of $R_1 \rightarrow M_1$ and $A_2 \rightarrow M_2$ of sample aged for 4 hours were significantly separated by ~20 K. Knowing the fact that the stress-induced martensite transformation is dependent on testing temperature, these two different temperature deficits will cause the deformation to happen under the rule of mixture. Note that, the example of this rule of mixture deformation has been illustrated in Chapter 5. With the assumption that the volume of $R_1$-phase was higher than the $A_2$-phase prior to deformation, thus the stress level for the transformation will be more dominantly determined by the temperature deficit of $R_1 \rightarrow M_1$. It is found that the $R_1 \rightarrow M_1$ peak temperature of sample aged for 4 hours was higher than the sample aged for 8 hours. Therefore, the critical stress level to induce the martensitic transformation for the sample aged for 4 hours shall be lower than the sample aged for 8 hours, as well observed in Figure 6.28.

Figure 6.28: Tensile deformation of Ti-50.8at%Ni after isothermally aged at 623 K

Figure 6.29 shows the deformation behaviour of wires aged at 673 K for different times. All samples showed clear stress induced $B2 \rightarrow R$ transformation prior to the onset of the stress plateau associated with the stress-induced $R \rightarrow B19'$ martensitic transformation. Pseudoelasticity was only achieved from samples aged for 30 min and 1 hour. This was
clearly due to the shift of reverse transformation temperature to a higher degree in samples aged for 2 hours and longer, as affected by the ageing process (Figure 6.19). Comparing with the samples aged at 573 K and 623 K, obviously the maximum ageing time for preserving pseudoelasticity decreased with increasing ageing temperature. It is also noted that the critical stress level for sample aged for 4 hours has become higher again than the sample aged for 8 hours. This is clearly explained by the lower $R_1 \rightarrow M_1$ temperature of sample aged for 4 hours as compared to the sample aged for 8 hours (Figure 6.19). Thus, this phenomenon further verifies the justification made previously that the decrease of stress for the sample aged for 4 hours in Figure 6.25 was due to the temperature difference between the testing temperature and that of $R_1 \rightarrow M_1$. Although the $A_2 \rightarrow M_2$ temperature of the sample aged for 8 hours (Figure 6.19) was lower than that of the sample aged for 4 hours, which may elevate the critical stress level for the transformation, it was expected that the contribution of $A_2 \rightarrow M_2$ temperature of the sample aged for 8 hours to influence the stress level was too small due to the fact that its $A_2$-phase volume was much smaller than the $A_2$-phase volume in the sample aged for 4 hours. Furthermore, the $A_2 \rightarrow M_2$ temperature of the sample aged for 4 hours was also lower than the $R_1 \rightarrow M_1$ temperature of the sample aged for 8 hours.

![Figure 6.29: Tensile deformation of Ti-50.8at%Ni after isothermally aged at 673 K](image-url)
Figure 6.30 shows the deformation behaviour of wires aged at 723 K for different times. Pseudoelasticity was observed in the sample aged for 30 min. The sample aged for 1 hour exhibited partial pseudoelasticity. Samples aged for longer times showed no pseudoelasticity, as for the samples aged at lower temperatures. It is seen that the critical stress level of the sample aged for 24 hours was higher than the sample aged for 8 hours. This is due to the lower $R_1 \rightarrow M_1$ temperature of the sample aged for 24 hours as compared to the sample aged for 8 hours (Figure 6.21). Additionally, it could also be contributed by the presence of significant surface oxidation in samples aged for 24 hours.

![Graph showing tensile deformation](image)

**Figure 6.30:** Tensile deformation of Ti-50.8at%Ni after isothermally aged at 723 K

Figure 6.31 shows the deformation behaviour of the samples aged at 773 K for different times. No complete pseudoelasticity was achieved from any of these samples. Samples aged for 30 min and 1 hour showed partial recovery upon unloading. Samples aged for 8 hours and 24 hours exhibited plastic deformation without martensitic transformation. This suggests that these two samples have lost their martensitic transformation due to severe oxidation.
6.3.3 Effect of Ageing Time and Temperature on Transformation Stress

Figure 6.32 shows the effect of ageing time on the critical stress for the forward stress-induced transformation for samples aged at different isothermal temperatures. Note that the transformation stress for samples aged at 573 K for 15 and 30 minutes were stress-induced B2→B19’, while for all other samples the stresses represented the stress-induced R→B19’ martensitic transformation. It is seen that the critical stress decreased continuously with increasing time ageing for all ageing temperature. The decrease was more rapid during the early stages of ageing.

Figure 6.33 shows the effect of ageing time on the critical stress for the reverse stress-induced transformation for samples aged at different isothermal temperatures. Ageing at 573 K produced a good progressive linear stress decrease with ageing time. Ageing at higher temperatures caused less pseudoelastic recovery at this testing temperature, thus the effect of ageing time is less quantifiable. However, it is seen that the negative gradient of the stress drop with respect to ageing time increased continuously as the ageing temperature increased.
Figure 6.32. Effect of ageing time on forward stress-induced transformation

Figure 6.33. Effect of ageing time on reverse stress-induced transformation

Figure 6.34 shows the effect of isothermal ageing temperature on critical stress for the forward stress-induced R→B19’ martensitic transformation for samples aged at different times. It is seen that the stress decreased with increasing ageing temperature.
Short time ageing is good to produce almost linear dependences of stress on ageing temperature. Ageing for 24 hours is not good in producing gradient stress levels.

![Figure 6.34. Effect of ageing temperature on forward stress-induced transformation](image)

Figure 6.34. Effect of ageing temperature on forward stress-induced transformation

Figure 6.35 shows the effect of isothermal ageing temperature on critical stress for reverse stress-induced martensitic transformation for samples aged at different times. It is seen that the stress level decreased with increasing ageing temperature. Short time ageing is good to produce almost linear decrease of stress with respect to the increase of ageing temperature. Ageing for more than 2 hours is not good in producing pseudoelastic recovery at this testing temperature.
6.3.4 Effect of Ageing Time and Temperature on Transformation Strain

Figure 6.36 shows the effect of ageing time on the forward transformation strain for samples aged at different isothermal temperatures. It is seen that, for short time ageing, the transformation strain decreased rapidly with increasing ageing time and remained constant after 8 hours. Transformation strain from low temperature ageing was always higher than that from high temperature ageing for all ageing time.

Figure 6.37 shows the effect of ageing temperature on the forward transformation strain for samples aged at different times. It is seen that for all ageing times, the transformation strain decreased with increase of ageing temperature, for low ageing temperatures (below 673 K). At above 673 K, the transformation strain became less sensitive to ageing time.
6.3.5 Gradient Ageing

Utilising the data presented in Figures 6.32 and 6.34, schematic illustrations can be generated to predict the “gradient stress plateau” of the martensitic transformation that can be produced from gradient ageing treatment. Unlike gradient annealing, gradient ageing can be done in two different ways: (a) gradient temperature and (b) gradient...
time. Figure 6.38 shows the schematic deformation behaviour of long wires aged at gradient temperature along its length, for different set of times. Figure 6.39 shows the possibility to produce a similar effect by ageing a wire at isothermal temperature but with gradual increase of ageing time along its length.

Figure 6.38 demonstrates that the start of the forward stress-induced transformation plateau is represented by the deformation of the high temperature end of the wire, and the end of the plateau represents the deformation of the low temperature end of the wire. It is noted that the gradient temperature ageing for the shortest period yields the lowest slope of stress gradient, but the magnitude of the stress is the highest. Additionally, the transformation plateau strain is also the longest. On the other hand, prolonging the ageing period will increase the slope of the stress gradient but at the reduction of transformation plateau strain. The reduction of plateau strain with respect to ageing time illustrated here is interpolated from Figure 6.36. The gradient stress window ($\Delta\sigma$) is highly dependent on and dictated by the range of the temperatures used for the ageing. For an example, Figure 6.34 shows that ageing at high temperature for prolonged time is not good for generating linear stress drop for the stress-induced martensitic transformation.

![Figure 6.38. Achievable gradient stress plateau from gradient temperature ageing treatment](image)
In Figure 6.39, the stress-induced transformation at the end of the longest ageing time occurs at the start of the stress plateau and that at the end of the shortest ageing time occurs at the end of the stress plateau. Increasing the ageing temperature causes the slope of the gradient plateau stress to increase but the transformation plateau strain to decrease. It is also demonstrated that the decrease of transformation plateau strain by the increase of ageing temperature is less than that by the increase of ageing time (Figure 6.38). The magnitude of gradient stress window ($\Delta\sigma$) is quantified by the range of gradient ageing time selected. As evident in Figure 6.32, over ageing may happen for treatment longer than 8 hours, thus produces less effect on martensitic transformation.

![Figure 6.39](image-url)

Figure 6.39. Achievable gradient stress plateau from gradient time ageing treatment

Tables 6.2 and 6.3 list the range of forward stress windows that are possibly to be produced from gradient temperature ageing and gradient time ageing, respectively. These values are extracted from Figures 6.32 and 6.34. The selection of gradient temperature range for ageing in Table 6.2 is based on the good linearity slope of forward stress change with respect to ageing temperature (Figure 6.34). Expending the temperature to above 723 K for ageing for 4 hours and 8 hours did not show continuous trend of stress drop as the temperature increases. Therefore, having a wire with a section that has been aged at above 723 K will not contribute to a good transformation “gradient stress plateau”. Similarly, a good stress gradient plateau for 24 hours of ageing is limited to only 573 – 673 K range of gradient temperature. The same approach is also
used in selecting the appropriate range of gradient ageing time when ageing the sample at any of the isothermal temperature (Table 6.3). Note that the reverse stresses are not included in these tables due to limited pseudoelasticity achieved from the samples at this testing temperature.

<table>
<thead>
<tr>
<th>Ageing Time (hr)</th>
<th>Stress Window (MPa)</th>
<th>Gradient Temperature Range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>112</td>
<td>573 – 773</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>573 – 773</td>
</tr>
<tr>
<td>2</td>
<td>122</td>
<td>573 – 773</td>
</tr>
<tr>
<td>4</td>
<td>122</td>
<td>573 – 723</td>
</tr>
<tr>
<td>8</td>
<td>143</td>
<td>573 – 723</td>
</tr>
<tr>
<td>24</td>
<td>80</td>
<td>573 – 673</td>
</tr>
</tbody>
</table>

Table 6.3. Attainable forward gradient stress window from gradient time ageing

<table>
<thead>
<tr>
<th>Ageing Temperature (K)</th>
<th>Stress Window (MPa)</th>
<th>Gradient Time Range (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>573</td>
<td>118</td>
<td>0.5 – 24</td>
</tr>
<tr>
<td>623</td>
<td>103</td>
<td>0.5 – 24</td>
</tr>
<tr>
<td>673</td>
<td>133</td>
<td>0.5 – 24</td>
</tr>
<tr>
<td>723</td>
<td>111</td>
<td>0.5 – 8</td>
</tr>
<tr>
<td>773</td>
<td>21</td>
<td>0.5 – 4</td>
</tr>
</tbody>
</table>

Figure 6.40 shows the actual deformation behaviour of Ti-50.8at%Ni wires that have been aged at gradient temperature range of 573 – 773 K for 2 hours. Deformation behaviour of the solution treated sample is also included for direct comparison. The wires were deformed at three different temperatures: 295 K, 318 K and 333 K, with each deformation using a fresh sample to avoid the effect of cycling. The sample deformed at 295 K showed the presence of R-phase transformation at the early stage of deformation. This corresponds well with the deformation behaviour of isothermally aged samples shown in Figures 6.27 and 6.28. Stress-induced $\text{R}\rightarrow\text{B19'}$ martensitic transformation began at ~260 MPa and the stress continuously increased to a maximum...
of ~450 MPa, thus yielded a positive stress gradient of 190 MPa. The transformation plateau strain achieved was ~7.5%. Partial recovery was achieved upon unloading. Deformation at higher temperatures improved strain recovery but caused the gradient stress plateau slope to decrease slightly. A close observation indicated that the change of plateau slope was mainly due to less effect of temperature dependence of stress-induced transformation from the low temperature end of the wire. Similar phenomenon was also observed in gradient annealed samples.

![Stress-Strain Curve](image)

Figure 6.40. Deformation behaviour of a wire after gradient temperature ageing for 2 hours (courtesy of Andrew King)

### 6.4 Discussion

#### 6.4.1 Functionally Graded NiTi from Gradient Temperature Annealing

**6.4.1.1 Martensitic Transformation Temperature Dependence of Stress-Induced Transformation**

As seen in Figure 6.9, the recrystallisation temperature of the Ti-50.5at%Ni alloy used is ~850 K. The range of the annealing temperature used for gradient anneal is entirely below this temperature. In this regard, the annealing is considered partial anneal, as opposed to a full recrystallisation anneal. Partial anneal has two effects on the alloy: (1) to increase the mechanical resistance of the matrix to deformation (including both plastic deformation and deformation via martensitic transformation), in other words, to
increase the critical stress for slip and the critical stress to induce martensitic transformation at a given temperature, and (2) to change the critical temperature for the martensitic transformation. One special point needs to be emphasized, which is the distinction between the B2→B19’ and R→B19’ transformations, or between \( T^{\text{AM}} \) and \( T^{\text{RM}} \), which have been commonly referred to simply as \( M_s \) in the literature. Both effects directly influence the critical stress for stress-induced martensitic transformation at a given deformation temperature.

It is seen in Figure 6.9 that the critical temperature of the forward R→B19’ martensitic transformation decreased with decreasing anneal temperature in region I. This observation is in good agreement with previous studies [11]. The effect of \( T^{\text{RM}} \) on the critical stress for stress-induced R→B19’ transformation is expressed in a Clausius-Clapeyron type equation [18], as:

\[
\frac{d\sigma}{dT}^{\text{RM}} = -\frac{\rho \Delta H^{\text{RM}}}{T^{\text{RM}} \varepsilon^{\text{RM}}} = k
\]  

(6.2)

which leads to

\[
\sigma^{\text{RM}}_{\text{therm}}(T) = k(T - T^{\text{RM}})
\]

(6.3)

It is also known that the resistance of the matrix to deformation increases with decreasing annealing temperature [13]. An increase in the matrix’s mechanical resistance directly enhances the external stress required for stress-induced transformation. Combine the above two effects, the critical stress for inducing martensitic transformation, as previously elaborated in Chapter 4, may be expressed as:

\[
\sigma^{\text{RM}}(T) = \sigma^{\text{RM}}_{\text{therm}} + \sigma^{\text{RM}}_{\text{mech}} = k(T - T^{\text{RM}}) + \sigma^{\text{mech}}
\]

(6.4)

The first term expresses the thermodynamic resistance to the stress-induced martensitic transformation at a given temperature and the second term expresses the mechanical resistance of the matrix. In this equation, \( T^{\text{RM}} \) is a function of the anneal temperature at below the recrystallisation temperature. This equation implies that annealing in a temperature gradient can be used as an effective means to create Ni-Ti materials with
functional gradients of transformation temperatures and stresses, as demonstrated in Figures 6.9 and 6.10.

6.4.1.2 Positive Gradient of Transformation Stress Plateau

The implication of a “gradient stress plateau” for the stress-induced martensitic transformation is significant. It is known that tensile deformation of thin wire samples of Ni-Ti via either stress-induced martensitic transformation or martensite variant reorientation proceeds over a stress plateau in localised “Lüders-type” manner [130-132, 185]. The positive linear stress gradient for the stress-induced transformation is the first of the kind reported. Such behaviour is advantageous for load-controlled actuation in applications.

In addition, it is evident that the gradient of the “plateau stress” can be altered to any required stress interval by adjusting the temperature range for the gradient annealing, as demonstrated in Figures 6.12 and 6.13. This work demonstrates a feasible technique for producing continuous microstructure gradient with gradient functional behaviour. Figure 6.16 also demonstrates that the gradient microstructure produced from the gradient temperature annealing successfully exhibits good pseudoelastic cycle with constant positive plateau stresses on both the forward and the reverse transformations. The transformation strain achieved for the cycle deformation may reach up to ~7.5%.

One other aspect that needs to be considered in designing for functionally graded Ni-Ti by means of gradient anneal is the yield strength of the material. It is known that the yield strength of near-equiaxial Ni-Ti decreases with increasing annealing temperature in the range below the recrystallisation temperature [120]. Given the fact that the critical stress for inducing the martensitic transformation increases with decreasing annealing temperature, it is obvious that the limit of the width of the temperature window for the gradient anneal is such that the yield strength of the material at the high-anneal-temperature end is greater than the critical stress for inducing the martensitic transformation at the low-anneal-temperature end; otherwise the stress-induced transformation at the low-anneal-temperature end will be prohibited by the occurrence of plastic deformation at the high-anneal-temperature end and thus the material wasted.
6.4.2 Functionally Graded NiTi from Gradient Ageing Process

6.4.2.1 Effect of Ageing on Transformation Behaviour

It is evident that the thermal transformation behaviour of Ti-50.8at%Ni is sensitive to ageing treatment, as shown in Figures 6.17 – 6.23. The transformation behaviour exhibits complex responses to ageing, including the suppression of the original B2→B19’ transformation, the appearance of the B2→R transformation, the development of the B2→R→B19’ transformation, the occurrence of the “multi-stage” transformation, and the restoration of the B2→B19’ transformation at higher temperatures.

There have been extensive discussions in the literature about the detailed mechanisms of these complex transformation behaviours, and not all explanations are received with equal level of acceptance. In general, the main view points may be summarised as following.

1. Suppression of the original B2→B19’ transformation (A0→M0): This occurs in the very early stage of ageing, before the full development of the R-phase. This has been attributed to the atomic shuffling as a precursor stage to forming the GP zones and precipitates [121].

2. Appearance of the R-phase: It is well established that the appearance of the R-phase results from the formation of coherent Ti3Ni4 precipitates [110, 157, 158, 192]. The early appearance of the R-phase during ageing is often not followed by the R→B19’ transformation [121].

3. Occurrence of B2→R→B19’ transformation: This behaviour follows in the next stage of ageing from the behaviour above. The R→B19’ transformation appears from very low temperature and moves up gradually to higher temperatures. There is a lack of clear explanation of this process, but the gradual reduction of the Ni content in the matrix due to growth of Ti3Ni4 precipitates is a logical contributor [25, 110, 121, 158, 174].

4. Multiple stage transformation behaviour: The multiple stage transformation behaviour may manifest in several different forms, including 2-stage B2→R transformation [149, 193], 2-stage R→B19’ transformation [151, 155], and concurrent occurrence of B2→R→B19’ and B2→B19. This is generally attributed to the inhomogeneity of the type and distribution of coherent precipitates.
(5) Restoration of the B2→B19’ transformation: This generally occurs after ageing at high temperatures over long periods of time. This is attributed to the formation of large incoherent Ti$_2$Ni$_3$ precipitates [121]. This obviously corresponds to the over-aged state. This phenomenon is shown in Figures 6.21 and 6.23, where the A$_2$↔M$_2$ transformation peak was detected at higher temperature than the original A$_0$↔M$_0$ peak. It is also evident that the A$_2$↔M$_2$ transformation peak temperature and size continuously increased as the ageing time and temperature increased. This signifies the increase of Ni-depleted volume near the incoherent precipitate.

Whereas most of these ageing induced transformation phenomena may be explained by the changes in precipitate type, coherency and distribution and the change in matrix composition, there does not exist one simple and common underlying metallurgical mechanism responsible for these changes, thus the absence of a common dependence of critical transformation temperatures on ageing conditions. For each particular transformation, a simple dependence may be recognised, as seen in Figures 6.24 and 6.25, the multiplicity of the transformations prevents a common trend to be identified. This makes it difficult to design functionally graded NiTi via ageing treatment based on thermal transformation measurement.

6.4.2.2 Effect of Ageing on Deformation Behaviour

It is evident that the mechanical behaviour of the stress-induced martensitic transformation of Ti-50.8at%Ni is also sensitive to ageing treatment, as shown in Figures 6.32 - 6.37. It is evident that all samples showed relatively simple deformation process involving a minor stage of stress-induced B2→R followed by a major stage of R→B19’ over a stress plateau or direct B2→B19’ transformation. It is generally observed that both the critical stress for inducing the martensite (from either the R-phase or the B2-phase) and the transformation strain decrease with increasing ageing time and temperature. This provides the basis for using ageing as a means to create functionally graded NiTi. At the meantime, the yield strength decreases as the ageing temperature increases [194]. Considering both stresses, a good temperature range for gradient ageing for Ti-50.8at%Ni is identified to be 573 – 723 K. The plateau stress gradient for the stress-induced forward transformation of the sample deformed at 295 K is 2.5 GPa over a stress window of 190 MPa.
6.4.2.3 Correlation Behaviour between Thermal and Mechanical Transformations

It is evident in the experimental evidences obtained and the discussions presented above that there is a lack of direct correlation between the behaviour of the thermally induced transformations and the mechanically induced transformations, in particular lack of correlation between the critical stress for inducing the martensitic transformation and the critical temperature of the thermally induced transformations. Mechanically, a B2→B19’ transformation may be induced in a sample that exhibits only a B2→R→B19’ transformation behaviour without the B2→B19’ transformation, as seen in Figure 6.17. Also samples showing multiple stage thermal transformation behaviour always exhibit only a single stage stress-induced transformation, for example the samples in Figure 6.21. This implies that it is inappropriate, or impossible, to predict and design a functionally graded mechanical behaviour based on thermal transformation behaviour.

6.4.3 Comparison between Gradient Annealing and Gradient Ageing

A comparison between the effects of annealing and ageing on yield strength and critical stresses for inducing martensitic transformation is illustrated in Figure 6.41. The effects of annealing ($\sigma_y^{\text{anl}}$, $\sigma_{\text{fwd}}^{\text{anl}} (295K)$ and $\sigma_{\text{fwd}}^{\text{anl}} (313K)$) are regenerated from Figure 6.5 for the Ti-50.5at%Ni alloy. The effect of ageing on the forward stress-induced transformation ($\sigma_{\text{fwd}}^{\text{age}} (295K)$) is regenerated from Figure 6.34 for the Ti-50.8at%Ni sample aged for 1 hour. The effect of ageing temperature on the yield strength ($\sigma_y^{\text{age}}$) of Ti-50.8at%Ni is interpolated from reference [194]. The difference between the higher end and the lower end of the critical stress curve for inducing martensite is the maximum stress interval achievable for functionally graded NiTi. It is seen that ageing treatment has less effect on increasing the maximum interval of the critical stress for transformation than annealing. The maximum stress interval achievable for gradient annealing is 270 MPa and that for gradient ageing is 190 MPa. At the meantime, the yield strength exhibited similar response to the two treatments.
Figure 6.41. Comparison of the effect of annealing and ageing temperature toward yield strength and critical stresses for inducing martensitic transformation.
CHAPTER 7

CONCLUSION AND FUTURE RESEARCH

This study investigated three main aspects of thermomechanical treatments of near-equiatomic Ni-Ti shape memory alloys, including (i) the effect of cold work percentage and partial anneal on thermal and mechanical behaviours of the alloy, (ii) the phenomenon of heat treatment induced oxidation and Ti-depletion, and (iii) design and creation of functionally graded NiTi by means of gradient heat treatment. The main conclusions of this study may be summarised as following.

7.1 Cold Work and Partial Anneal

This work is conducted on a Ti-50.5at%Ni. The main findings include the following.

1-1 Severe cold working suppresses the $B_2 \rightarrow B19'$ martensitic transformation and introduces the $B_2 \rightarrow R$ transformation. Cold working also widens transformation temperature intervals, implying inhomogenization of the matrix. Partial anneal at below the recrystallisation temperature restores the transformations. The temperature of the $R \rightarrow B19'$ transformation increases with increasing anneal temperature. These observations confirm with previous published findings in the literature.

1-2 The critical stresses to induce the martensitic transformation decrease with annealing temperature. The effect of prior cold work is fully eliminated by full recrystallisation anneal.
1-3 The critical stresses to induce the martensitic transformation increase with increasing the level of the prior cold work for a given anneal temperature below the recrystallisation temperature. The difference caused by the different levels of cold work is more prominent for low annealing temperatures.

1-4 The effective range of cold working for optimum effects on martensitic transformation behaviour is 50% - 70% by elongation.

1-5 The mechanical resistance to stress-induced transformation remains constant irrespective of the percentage of cold work for all the partial anneal temperatures. The increase of transformation stress is mainly caused by the suppression of the transformation temperatures, particularly that of B2→B19'. This allows easy design of mechanical properties of NiTi based on thermal transformation behaviour.

1-6 The magnitude of deformation-induced martensite stabilisation increases with increasing annealing temperature. A maximum stabilisation effect of ~30 K is achieved from fully recrystallised samples and the minimum is practically zero for samples annealed at below 623 K.

The effect of the magnitude of cold work has largely been neglected in the literature. This study provides a complete data set of the effect of severity of cold work and its impact on partial anneal of NiTi. Such data is of practical use for NiTi materials production and quality control.

7.2 Oxidation and Titanium Depletion

This study is conducted on Ti-50.5at%Ni. The temperature range for the heat treatment is 873 – 1223 K. The heat treatment is done in argon and in air. The main findings are as following.

2-1 Heat treatment in air induced the formation of complex multiple layers on the surface of NiTi. Oxidation occurred by preferential leaching of Ti from the NiTi matrix and the layers are formed sequentially. Low temperature and short
exposure time in air causes the formation of a thin TiO$_2$ layer on the surface. Enrichment of Ni underneath the surface TiO$_2$ layer causes the formation of a second layer of TiNi$_3$. Prolonged exposure at high temperatures induces formation of a composite layer of TiO$_2$ and Ni(Ti) in between the surface TiO$_2$ layer and the underneath TiNi$_3$ layer. Beneath the TiNi$_3$ layer in the matrix, there is a region with depleted Ti, essentially enriching the matrix to be rich in Ni.

2-2 The initial stage of diffusional process of the oxidation follows the chemical reaction of $3\text{NiTi} + 2\text{O}_2 = \text{TiNi}_3 + 2\text{TiO}_2$. As the supply of free Ti atoms at the interface decreases due to oxide thickness barrier eventually forces the oxidation to take a different route via the decomposition of TiNi$_3$, as expressed in the reaction of $\text{TiNi}_3 + \text{O}_2 = 3\text{Ni(Ti)} + \text{TiO}_2$.

2-3 Oxidation is negligible for heat treatment in air at below 873 K, even for 24 hours of exposure. This signifies that the recrystallisation process is acceptable to be carried out in air since the temperature range for near-equiatomic NiTi alloy system is ~850 K. Heating the sample in air to above 1000 K and for prolonged period causes severe oxidation and Ti depletion. The oxidised samples show diminished martensitic transformation latent heat. Removal of oxidised layers restores the full magnitude of the latent heat measured.

2-4 Heat treatment in argon is able to avoid the formation of oxide even at the extreme temperature of 1223 K and for 24 hours. However, the thermal transformation and mechanical behaviour of the alloy were still significantly affected by the depletion of Ti near the surface region.

2-5 The oxide-related surface layers exhibits no martensitic transformation, thus do not contribute to the shape memory effect. The Ti-depleted zone may exhibit martensitic transformation in the region adjacent to the original matrix, but gradually loses its ability to transformation when the local Ni content increases to above a threshold toward the interface with the TiNi$_3$ layer, and act as a passive metal. These oxide-related surface layers and the Ti-depleted zone increase the mechanical resistance to stress induced martensitic transformation and hinders the recovery of shape change in pseudoelasticity.
7.3 Functionally Graded NiTi by Gradient Annealing

Annealing in a gradient temperature field is applied to Ti-50.5at%Ni to create functionally graded NiTi. The main findings may be summarised as following.

3-1 The gradient anneal is effective in creating wires or rods of near-equiatomic NiTi alloys with varying deformation behaviour along their length, in particular with varying levels of the critical stress for inducing the martensitic transformation at a given temperature.

3-2 The effective temperature range for gradient anneal for functionally graded Ti-50.5at%Ni is 600 – 800 K. The effective temperature range for functionally graded pseudoelastic Ti-50.5at%Ni is 630 – 783 K.

3-3 The effective temperature range for gradient anneal is dependent and limited by the transformation stress, which is testing-temperature dependent, and the yield strength. The criterion is that the transformation stress at a given temperature is lower than the yield strength. Generally lower application temperatures permit wider temperature ranges for gradient anneal.

3-4 Functionally graded NiTi created by gradient anneal exhibits unique “Lüders-type” deformation behaviour with a positive “gradient stress plateau”. The stress interval achieved for the Ti-50.5at%Ni alloy is 280 MPa for the stress-induced forward transformation and 300 MPa for the reverse transformation. The estimated plateau stress gradients for the stress-induced forward and reverse transformations are 4.7 GPa and 8.6 GPa, respectively.

3-5 The slope of the “gradient stress plateau” can be varied by selecting appropriate temperature ranges for the gradient anneal. The gradient Lüders-type deformation provides the possibility for gradual actuation under load control.

3-6 The gradient microstructure produced from the gradient temperature annealing successfully exhibits good pseudoelastic cycle with constant positive plateau stresses on both the forward and the reverse transformations. The transformation strain achieved for the cycle deformation may reach 7.5%.
The implication of a “gradient stress plateau” for the stress-induced martensitic transformation is significant. The positive linear stress gradient for the stress-induced transformation is the first of the kind reported. Such behaviour is advantageous for load-controlled actuation in applications.

7.4 Functionally Graded NiTi by Gradient Ageing

Ageing in a gradient temperature field is applied to Ti-50.8at%Ni to create functionally graded NiTi. The main findings may be summarised as following.

4-1 A full set of experiment on the effects of time and temperature of ageing on thermal transformation behaviour of Ti-50.8at%Ni is completed. The transformation behaviour is found to evolve through several stages with increasing the intensity of ageing, including the suppression of the original B2\(\rightarrow\)B19’ transformation during the very early stage of ageing, the appearance of the B2\(\leftrightarrow\)R transformation, the development and evolution of the B2\(\rightarrow\)R\(\rightarrow\)B19’ transformation, the occurrence of the “multi-stage” transformation, and the restoration of the B2\(\leftrightarrow\)B19’ transformation at higher temperatures with over-ageing. These findings agree with previous studies published in the literature, and provide a comprehensive dataset of reference for the design of functionally graded NiTi by ageing.

4-2 A comprehensive set of experiment on the effects of time and temperature of ageing on the mechanical behaviour of the stress-induced martensitic transformation is also completed. Despite the complexity of the thermal transformation behaviour, aged Ti-50.8at%Ni samples all deformed via stress-induced B2-R\(\rightarrow\)B19’ or B2\(\rightarrow\)B19’. The critical stress for the apparent stress plateau and the transformation strain decrease with increasing ageing time and temperature. Yield strength also decreases as the ageing temperature increases.

4-3 There is no clear correlation between the critical temperatures of thermally induced transformations and the critical stresses of the mechanically induced transformations for the aged samples. This means it is inappropriate to predict the behaviour, or to design the heat treatment process based on the thermal transformation behaviour, for functionally graded NiTi.
Considering both stresses, a good temperature range for gradient ageing for Ti-50.8at%Ni is 573 – 723 K. For deformation at 295 K, gradient-aged Ti-50.8at%Ni exhibits a positive transformation stress gradient of 2.5 GPa over a stress window of 190 MPa during stress-induced martensitic transformation.

Ageing treatment has less effect on increasing the maximum interval of the critical stress for transformation than annealing. The maximum stress interval achievable for gradient annealing is 270 MPa and that for gradient ageing is 190 MPa. At the meantime, the yield strength exhibited similar response to the two treatments.

These findings demonstrate that the gradient ageing is novel technique for producing functionally graded Ni-Ti.

**7.5 Suggestion for Future Research**

Most studies presented above are considered complete. The only major work that requires continuation is the functionally graded NiTi. In this regard the following may be suggested.

5-1 This study has demonstrated the feasibility of using gradient ageing and gradient annealing to produce functionally graded NiTi. This is a preliminary study and the technique needs to be optimised.

5-2 Response to ageing is specific for each NiTi of different Ni contents. Therefore, complete data for each alloy is needed. Data on transformation behaviour after ageing is reasonably available in the open literature. Data on mechanical behaviour is scarce.

5-3 NiTi is generally recognised as being reasonably resistant to fatigue. However due to the gradient stress slope, it is expected that one side of the sample may have a lower endurance limit due to elastic/plastic deformation of the martensite. Therefore, the long-term affects in functionally graded NiTi should be investigated as it may have implications for actuator design using functionally graded NiTi.
REFERENCES


List of Publications


