PSEUDOELASTICITY AND CYCLIC BEHAVIOURS OF NICKEL-RICH NiTi SHAPE MEMORY ALLOY

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PSEUDOELASTICITY AND CYCLIC BEHAVIOURS OF NICKEL-RICH NiTi SHAPE MEMORY ALLOY

by

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LIST OF ABBREVIATIONS

SMA	Shape Memory Alloy
DSC	Differential scanning calorimeter
NiTi	Nickel titanium
UTM	Universal Tensile Machine
ASTM	American Society for Testing Materials

LIST OF SYMBOLS

%	Percentage
B2	Austenite phase
B19’	Martensite phase
M_s	Martensite start temperature
M_f	Martensite finish temperature
M_p	Martensite peak temperature
A_s	Austenite start temperature
A_f	Austenite finish temperature
R	R-phase
M_d	Plasticity start temperature
η_{AM}	Thermal hysteresis austenite to martensite
ΔT_{fwd}	Temperature interval of forward transformation
ΔT_{rev}	Temperature interval of reverse transformation
Δh	Heat flow
σ_{cri}	Critical transformation stress
σ_y^M	Martensite yield strength
σ_y^A	Austenite yield strength
ε_t	Transformation strain
ε_r	Residual strain
GB	Grain boundary
GI	Grain interior
I	Ratio of nucleation rate

SIFAT PSEUDOELASTIK DAN KITARAN ALOI INGATAN BENTUK NiTi KAYA NIKEL

ABSTRAK

NiTi yang hampir equiatom adalah salah satu aloi ingatan bentuk yang terkenal yang digunakan dalam pemencilan getaran dan aplikasi peredaman. Ini disebabkan oleh sifat pseudoelastiknya. Pesudoelastik merujuk kepada keupayaan aloi ingatan bentuk untuk segera pulih daripada ubah bentuk yang besar selepas beban ubah bentuk dilepaskan. Bagaimanapun, kekuatan alah aloi ini rendah sehingga terdedah kepada kehelan setempat. Dalam hal ini, mengekalkan sifat pseudoelastik aloi menjadi satu cabaran. Aloi terdegradasi yang melibatkan penumpukan sisa terikan yang progresif dan pengurangan terhadap transformasi tegasan apabila dikenakan kepada kitaran beban. Rawatan penuaan digunakan secara meluas untuk meningkatkan kekuatan alah aloi melalui pengerasan mendakan. Hanya mendakan yang koheren yang benar-benar dapat meningkatkan kekuatan alah. Juga, pengerasan mendakan ini adalah lebih berkesan kepada NiTi yang tinggi kandungan Ni. Kesan penuaan ini terhadap kekuatan alah dan rintangan kelesuan fungsian aloi kurang diterokai terutamanya untuk komposisi atas 51at%Ni. Kajian ini bertujuan untuk mengukur kesan penuaan aloi NiTi kaya-Ni terhadap kekuatan alah dan sifat pseudoelastik. Respons kekuatan alah terhadap prestasi kitaran NiTi kaya-Ni juga disiasat.

Aloi NiTi yang komersial dengan komposisi Ti-51at% Ni dan Ti-50.8at% Ni telah digunakan dalam kajian ini. Kerja-kerja eksperimen melibatkan rawatan penuaan isoterma pada julat suhu 400°C hingga 550°C selama 15, 30 dan 60 minit selepas sahaja rawatan larutan pada suhu 900°C. Analisis termal dilakukan menggunakan Calorimetry Scanning Differential (DSC) untuk menentukan suhu transformasi fasa. Ujian tegangan pada suhu bilik dilakukan untuk mengenal pasti sifat pseudoelastik, kekuatan alah dan prestasi kitaran menggunakan mesin tegangan universal (UTM).

Keputusan menunjukkan bahawa kekuatan alah meningkat apabila suhu penuaan bertambah, dan spesimen 51at%Ni yang dipanaskan pada 450°C selama 30 minit mencatatkan nilai tegasan alah martensite yang tertinggi. Rawatan penuaan di atas 500°C menyebabkan kekuatan alah menurun dengan ketara. Melalui perbandingan, spesimen 50.8at%Ni menunjukkan kekuatan alah yang lebih rendah daripada 51at%Ni. Sifat pseudoelastik spesimen yang dipanaskan didapati merosot dengan peningkatan tempoh rawatan penuaan. Aloi NiTi dengan komposisi 51at%Ni menunjukkan kurang daripada 1% terikan sisa yang tidak dikembalikan pada suhu bilik walaupun suhu selesai fasa austenit, A_f lebih tinggi daripada suhu semasa ujian dijalankan. Berbeza dengan 51at%Ni, spesimen 50.8at%Ni yang dipanaskan pada suhu 425°C hingga 500°C menunjukkan kebolehpulihan yang rendah dengan 2% terikan sisa. Sifat ubah bentuk kitaran aloi didapati lebih stabil untuk spesimen yang dipanaskan pada suhu penuaan yang lebih rendah. Penuaan pada suhu yang lebih tinggi (525°C dan 550°C) menyebabkan keterikan sisa meningkat dan transformasi tegasan berkurangan dengan ketara pada beberapa kitaran pertama yang menunjukkan kemerosotan sifat fungsian. Rawatan penuaan terhadap Ti-51at%Ni pada suhu 450°C selama 30 minit disyorkan sebagai keadaan penuaan terbaik untuk tujuan ubah bentuk kitaran. Ia menghasilkan tegasan alah martensit, σ_y^M yang tertinggi iaitu pada 1335 MPa, menunjukkan sifat pseudoelastik yang baik dengan terikan sisa, ε_r pada 0.41% dan rintangan kelesuan fungsian yang tinggi dengan perbezaan terikan sisa, $\Delta\varepsilon_r$ pada 0.08%.

PSEUDOELASTICITY AND CYCLIC BEHAVIOURS OF NICKEL-RICH NiTi SHAPE MEMORY ALLOY

ABSTRACT

Near-equiatomic NiTi is one of the famous shape memory alloys used in vibration isolation and dampening application. This is due to its pseudoelastic behaviour. Pesudoelasticity refers to the ability of shape memory alloy to instantly recover from very large deformation after the deformation load is released. However, the yield strength of this alloy is low thus susceptible to localized dislocation. In this regard, preserving the pseudoelasticity of the alloy becomes a challenge. The alloy degrades, involving progressive accumulation of residual strain and reduction of the transformation stress when subjected to cyclic loading. Aging treatment is widely used to improve the yield strength of the alloy through precipitation hardening. Only coherent precipitates can profoundly increase the yield strength. Also, the precipitation is more effective in high Ni content of NiTi alloy. The effect of ageing on the yield strength and functional fatigue resistance are less explored especially for composition above 51at%Ni. This study aims to quantify the ageing effect of Ni-rich NiTi alloy towards the yield strength and the pseudoelastic behavior. The response of the yield strength towards the cyclic performance of Ni-rich NiTi alloys is also investigated.

Commercial Ni-rich NiTi alloys with composition Ti-51at%Ni and Ti-50.8at%Ni were used in this study. The experimental works involved the isothermal ageing at a temperature range of 400°C to 550°C for 15, 30 and 60 minutes after solution treated at 900°C. Thermal analysis was done using Differential Scanning Calorimetry (DSC) to specify the phase transformation temperature. The tensile tests at room temperature were carried out to characterise the pseudoelasticity, yield strength and the cyclic performance using universal tensile machine (UTM).

The results show that the yield strength increased as the ageing temperature increased, and the specimen of 51at%Ni alloy aged at 450°C for 30 minutes recorded the highest martensite yield stress value. Ageing at above 500°C caused the yield strength to decrease significantly. By comparison, 50.8at%Ni specimens showed lower yield strength than 51at%Ni. The pseudoelasticity of the aged specimens was found to decrease with the increase of ageing times. NiTi alloy with 51at%Ni showed less than 1% unrecovered strain at room temperature even though the austenite finish temperature, A_f is higher than the testing temperature. Unlike 51at%Ni, 50.8at%Ni specimens aged at 425°C to 500°C showed poor recoverability with more than 2% residual strain. The cyclic deformation behaviour of the 51at%Ni alloy was found to be more stable for specimen aged at lower ageing temperature. Ageing at very high temperature (525°C and 550°C) caused the residual strain to increase and the transformation stress to decrease significantly over the first few cycles indicating functional behaviour degradation. Ageing of Ti-51at%Ni at 450°C for 30 minutes is recommended as the best ageing condition for cyclic deformation purpose. It produced the highest martensite yield stress, σ_y^M of 1335 MPa, performing considerably good pseudoelasticity with residual strain, ε_r of 0.41% and high functional fatigue resistance with residual strain difference, $\Delta\varepsilon_r$ of 0.08%.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Shape memory alloy (SMA) is a group of alloys that can remember to return to their original shape when deformed to beyond elastic region upon the removal of the load or the application of heat. This shape memory is the manifestation of martensitic phase transformation of the alloy that involves diffusionless reversible transformation of the phases between parent austenite and martensite (Barbarino et al., 2014; Mohd Jani et al., 2014). The phase transformation produces huge macroscopic strain amplitude of about 8-10% (Chan et al., 2012; Helbert et al., 2014). Figure 1.1 shows the stress-strain curve of shape memory alloy to illustrate the reversible transformation.

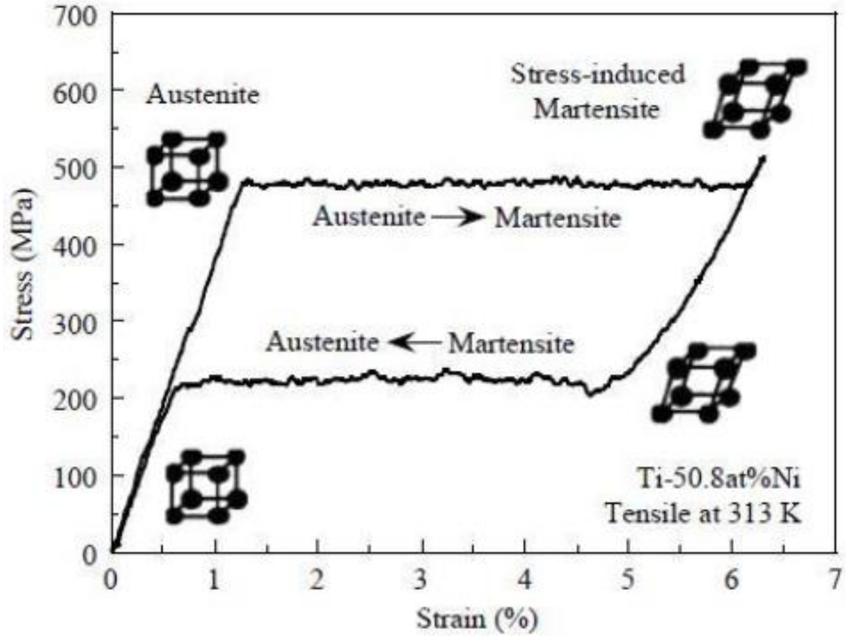

Figure 1.1. Stress-strain curve of reversible phase transformation of shape memory alloy (S. Jiang et al., 2017)

Shape memory alloy is temperature-dependent and very sensitive to alloy composition (Otsuka & Ren, 2005). The alloy can only recover its deformation instantaneously upon the removal of the load if the environment temperature is above its specific parent phase transformation temperature, namely austenite finish, A_f. This behaviour is called pseudoelastic. If the testing temperature is below A_f the alloy can only return to its original shape upon load removal if heated to above A_f. This behaviour is called shape memory effect. The difference between these two unique behaviours lies in a way the alloy recover its deformed shape as illustrated in figure 1.2 (Hodgson et al., 2002; Huang et al., 2010; Sun et al., 2012).

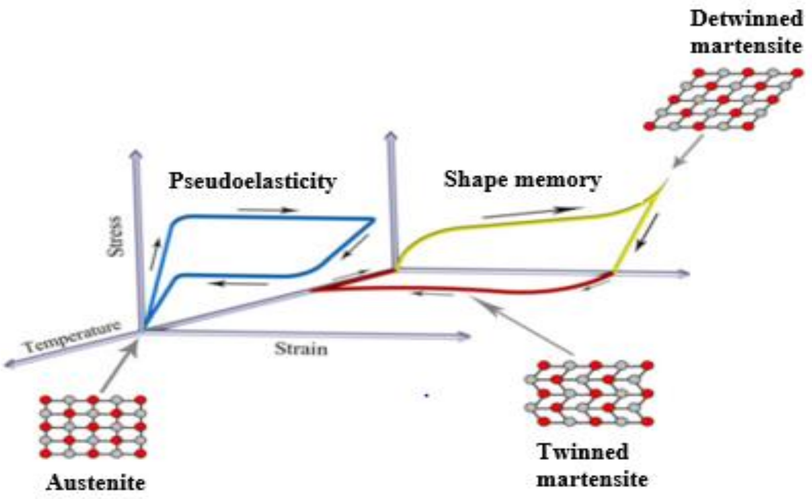

Figure 1.2**.** NiTi shape memory alloy deformation behaviour (Salehi et al., 2014)

Shape memory behaviour was initially observed in 1932s on Au-Cd alloy by Arne Orlander (Hassan et al., 2014). The alloy exhibited a unique deformation behaviour from the observation of formation and disappearance of a martensitic phase by increasing and decreasing the temperature. Since then immerse interest have been put on these alloys for its unique potential applications. More and more alloys systems have been found that also exhibit shape memory behaviours including copper-aluminium-nickel (Cu-Al-Ni), iron-manganese-silicon (Fe-Mn-Si), and copper-zincaluminium (Cu-Zn-Al) (Hodgson et al., 2002; Mohd Jani et al., 2014; van Humbeeck, 1997). Of all the alloys, NiTi and copper based alloys have received great popularity in research development and application due to high efficiency, good biocompatibility, high corrosion resistance and machinability (Barbarino et al., 2014; Mohd Jani et al., 2014).

Knowing that shape memory alloy exhibits large recoverable strain, engineers have seen the potential solution of these smart material in structural damage control. With substantial deformation recovery and high absorbing capacity can provide vibration isolation to a system. Intelligent passive devices for seismic control structure utilised shape memory alloy wires in the device called self-centring hybrid damper (SCHD). The devices use the NiTi alloy wire as the energy dissipation medium and core recentering components. The mechanism involves the combination of stress hysteresis loop of shape memory alloy and steel pipe to exhibit self-centring behaviour accompanied with high energy dissipation to mitigate vibration. This innovative damper system is effective in reducing structure dislocation, peak drift and acceleration of the seismically excited structure (Asgarian et al., 2016; Mohd Jani et al., 2014; Silva et al., 2015).

Despite providing large recoverable deformation strain, the alloys are susceptible to degradation when subjected to cyclic loading. This somehow limits the applicability of the alloy to relatively small usable strain (Mohd Jani et al., 2014). As reported, the recommended strain of SMAs is only 3-4% which is much lesser than their actual transformation strain with respect to design safety. Overstraining or overstressing the alloy decreases the durability and reliability of the alloy to relatively small number of cycles before reaching the yield point or the mechanical breakage. It was also found that NiTi alloy exhibited softening behaviour that reduces the strain amplitudes and also causes the transformation stress to decrease. In consequences, for long-term usage, functional fatigue can damage the structure and the whole device system. (Eggeler et al., 2004; Kang & Song, 2015; Norfleet et al., 2009).

A heat treatment like ageing through precipitation hardening increase the dislocation resistance of the alloy thus improve the alloy cyclic behaviour (Otsuka & Ren, 2005). As the precipitation occurs due to excess Ni, the ageing is more effective for higher Ni content of NiTi alloy. Therefore, higher yield strength can be obtained through a Ni-rich NiTi alloy. The combination of two factors, proper ageing and high Ni content of NiTi alloy that can optimise the yield strength may have a different effect on the pseudoelasticity and cyclic loading which are less emphasised in existing literature.

1.2 Problem statement

Preserving the pseudoelastic behaviour of NiTi shape memory alloy while having a large deformation strain under mechanical cyclic loading still becomes a major challenge. The alloy’s recoverability is very much determined by the environment temperature. The task becomes more complicated as the activating temperature, in this case the A_f increases upon deformation due to martensite stabilisation effect (Yinong Liu & Yang, 2007; Mahmud et al., 2008; X. Ren et al., 1999). Moreover, most cyclic application instruments like damper or absorber are operated in a constant temperature without additional heat that can support the recovery.

Many experimental works associated with mechanical cyclic loading reported the occurrence of degradation of shape memory behaviour involving the reduction of transformation stress and the accumulation of residual strain as shown in figure 1.3.

The stress hysteresis also decreases with cycles indicating regression in heat dissipation energy until it stabilises in the subsequent cycles. Although the stabilised cycles show complete recovery due to dislocation hardening effect, the transformation strain and stress are much lesser than the first cycle.

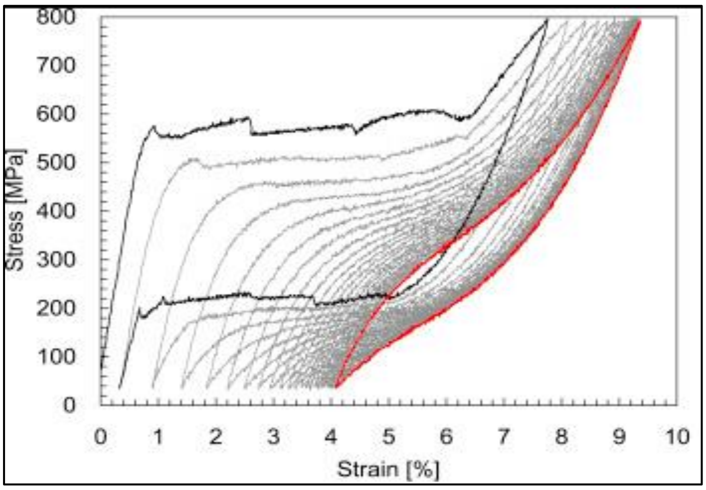

Figure 1.3 Degradation behaviour of NiTi subjected to cyclic loading (J. Wang et al., 2017)

Based on experimental findings, the inelastic mechanism is originated from the accumulation of residual martensite and the transformation-induced dislocation (J. Wang et al., 2017). Both mechanisms induced by localised slip propagation at the interface of austenite and martensite phase. It is resulted from the transformation stress that may be higher or closer to the austenite yield stress (Yu et al., 2015). However, most studies have only focused on investigating and predicting the fatigue life through many constitutive models (Kan & Kang, 2010; W. Ren et al., 2007; D. Song et al., 2016; Yu et al., 2015) rather than providing the solution.

Cyclic degradation of NiTi alloys is mainly caused by the inherent dislocation activities during martensite phase transformation. Therefore, increase the yield strength may lower the tendency for the alloy to slip. It is well established fact that ageing is a heat treatment that can strengthen the NiTi alloy through the precipitation hardening (Chiang et al., 2008; Otsuka & Ren, 2005). However, the ageing effect on cyclic behaviour towards alloy with higher Ni composition is less emphasised. Extensive study is required to investigate the changes in the yield strength and recoverability of the aged alloy under cyclic loading. The effect of ageing towards cyclic behaviour was studied by (Miyazaki et al., 1986) at different composition. The effect of precipitated NiTi alloy was also reported by (K Gall & Maier, 2002) using three different ageing temperatures in compression cyclic loading. However, the effect of ageing on the yield strength was not highlighted in both studies.

This study attempts to emphasize the significant of strengthening the alloy towards the cyclic performance through the application of ageing on high Ni-content of NiTi. Also, to provide an insight on the potential solution to enhance the alloy performance which therefore increase the workability of the alloy in a broad range of application especially in dampening and vibration control.

1.3 Objectives

The objectives of this study are:

1. To quantify the effects of ageing temperature and time toward yield strength, pseudoelasticity and cyclic behaviour of Ni-rich NiTi shape memory alloys.
2. To study the influence of the yield strength of Ni-rich NiTi alloys on the cyclic performance based on the evolution of the residual strain.

1.4 Scope of works

The scope of this work is fully experimental, based on common practice in this area. The Ni-rich alloys specimens used in this study were in the form of wires obtained from commercial supplier with composition of Ti-51at%Ni and Ti-50.8at%Ni.

The works carried out involved isothermal ageing treatment at temperature from 400°C to 550°C, and exposure time of 15, 30 and 60 minutes. This ageing treatment was done to quantify the ageing effect towards tensile deformation behaviour of the alloy.

The deformation behaviour analysed only tensile deformation at room temperature using universal tensile machine (UTM). Additionally, cyclic deformation behaviour was also analysed to quantify the effect of ageing on the cyclic performance. In cyclic test the specimens were subjected to 50 cycles of uniaxial quasi-static load.

Thermal transformation behaviour of aged samples was measured and analysed using Differential Scanning Calorimetry (DSC). This was done to determine the ageing effect towards martensitic transformation temperatures and the transformation pattern.

CHAPTER TWO

LITERATURE REVIEW

2.1 Martensite phase transformation of shape memory alloys

Shape memory alloys can exhibit martensitic phase transformation under the influence of heat, stress, electric and magnetic inputs (Brown et al., 2007; Z. Liu et al., 2011). Shape memory alloys consist of two primary state phases, the parent phase of austenite and the martensite. Martensitic phase transformation involves the reversible phase change between higher crystallographic symmetry of parent phase, austenite and lower symmetry phase of martensite exhibit thermoelastic transformation (J. Y. Liu et al., 2008). The phase transformation of austenite to martensite is a non-diffusive of solid-solid transformation as visualise in figure 2.1(a) (Lobo et al., 2015). The transformation is accompanied by large "shear-like" distortion resulted from rearrangement of the atomic lattice structure for sizeable inelastic deformation strain and recover by mean of load removal or upon application of heat (Frick et al., 2008).

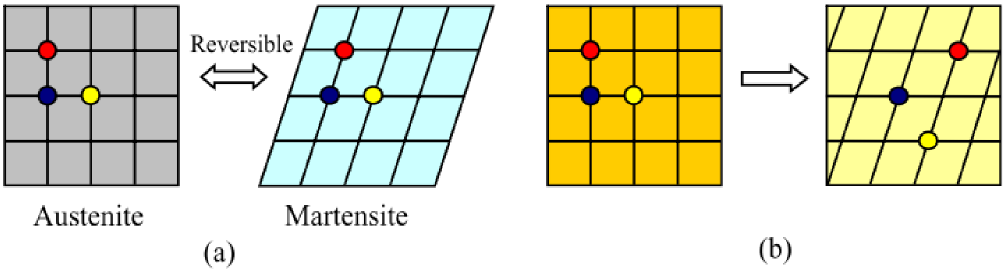

Figure 2.1. Schematic illustration to distinguish; (a) non-diffusive phase transformation and (b) diffusive phase transformation (Otsuka & Ren, 2005)

2.2 Thermomechanical behaviours of shape memory alloy

Thermoelastic martensitic transformation is a thermal and mechanical transformation system. Under different deformation temperature, shape memory alloy may exhibit different thermomechanical behaviour. The thermomechanical behaviour may also be complex corresponding to the influence of alloy’s composition and thermomechanical treatment (Karimzadeh et al., 2015; Yoshida et al., 2000).

2.2.1 Thermal transformation behaviour of shape memory alloys

The present temperature determines the microscopic phase and the deformation behaviour of shape memory alloy, it is essential to specify the activating temperatures for the phase transition to take place like the temperature where the austenite, B2 transforms to martensite, B19’ (Mischutta et al., 2006). Differential Scanning Calorimetry (DSC) is a commonly used method to monitor the phase transition temperature besides internal friction method and electrical resistance technique (Gallardo Fuentes et al., 2002; Abel et al., 2004). The instrument characterises the phase transformation temperature based on changes in the rate of heat flow through exothermic (cooling) and endothermic (heating) processes. Figure 2.2 represents the example of thermal transformation behaviour of a fully annealed NiTi alloy from DSC transformation window. Several parameters are conventionally defined as follows:

M_s: Martensite (B19’) starting temperature transformation

M_f: Martensite finish temperature transformation

A_s: Austenite (B2) starting temperature transformation

A_f: Austenite finish temperature transformation

η_{AM}: Thermal hysteresis of austenite to martensite transformation

ΔT_{fwd}: Temperature interval of forward transformation

ΔT_{rev}: Temperature interval for reverse transformation

Δh: heat change during transformation as determined by the area covered under the thermal peak in the spectrum

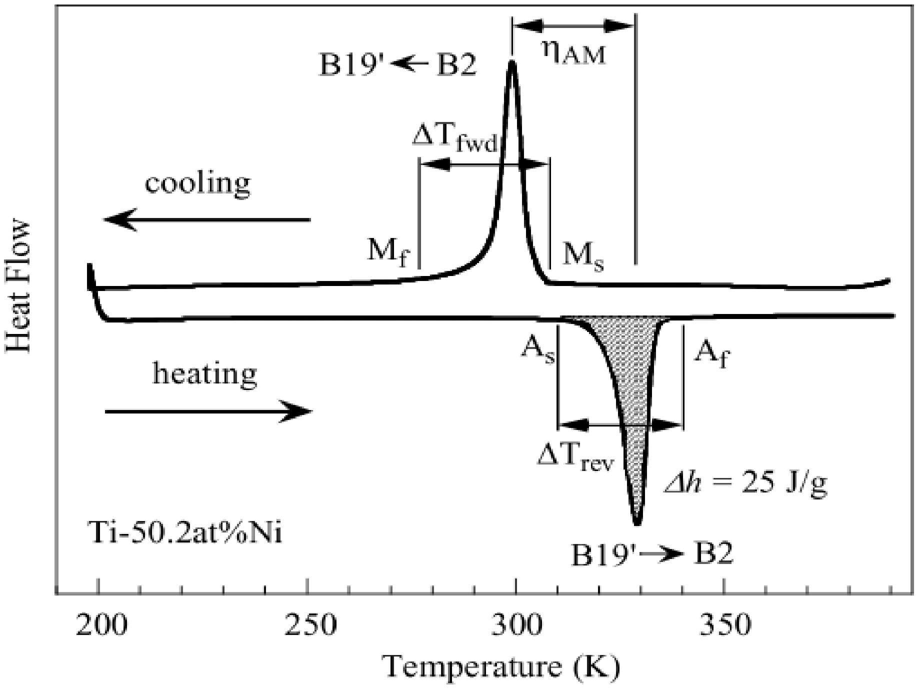

Figure 2.2. Thermal transformation behaviour of fully annealed of NiTi shape memory alloy (Mahmud et al., 2008)

2.2.2 Deformation behaviour of shape memory alloy

The deformation behaviour of shape memory alloy is practically presented through the stress-strain curve of tensile or compression loading. Figure 2.3 schematically demonstrates the typical tensile deformation behaviour of the pseudoelasticity shape memory alloy. The alloy is initially deformed in the austenite, B2 phase. The first stage of deformation in 2 involves linear elasticity of austenite. Like ordinary metal, the elastic strain at this stage can be described by classic Hooke's law of elasticity (G. Z. Wang, 2007). The forward transformation in 1 represents the transformation strain corresponds to the stress-induced martensitic transformation.

The critical transformation stress, σ_{cri} that initiates the transformation is a function of temperature in which it confirms the Clausius-Clapeyron relation. The relation describes a linear relationship between the transformation stress and the operating temperature. Increasing the temperature leads to increase the required stress for transformation to happen (Yinong Liu et al., 2008). The subsequent stage at 5 precedes with stress and strain increment for elastic deformation of detwinned martensite. Detwinned martensite is named as the martensitic transformation is induced by the input stress. It is non-linearity curve which somehow dislocations are potentially induced in the alloy matrix. The rapid production of plastic deformation occurs as the stress passing the martensite yield strength, $\sigma_y^M$of the alloy (X. Wang et al., 2008). Unloading at this stage leave a residual strain ε_r. The residual strain incorporates the transformation strain, (which may recover by heating) and permanent plastic strain.

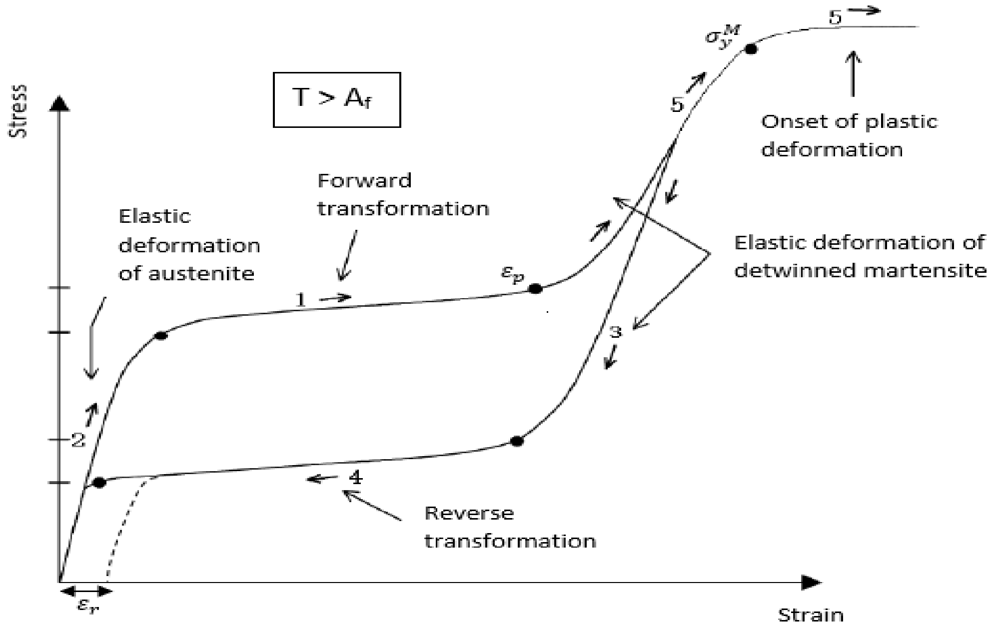

Figure 2.3. Tensile deformation behaviour of shape memory alloy (Dolce & Cardone, 2001)

2.2.3 Shape memory effect and pseudoelasticity

Fundamentally, shape memory alloy can exist in two different phases, austenite, B2 and martensite, B19’. However, at a given temperature and stress input, the lattice structure of the two phases would change at three different crystal structures, i.e twinned martensite, detwinned martensite and austenite. There are six possible transformations as illustrated in Figure 2.4 associated with these phases that contribute to the two unique behaviours, shape memory effect and pseudoelasticity (Mohd Jani et al., 2014; Wada & Liu, 2008).

Austenite structure is stable at high temperature, and the martensite structure is stable at low temperature. When a shape memory alloy is cooled at the martensite finish temperature, Ms, without the application of external stress, the structure transforms into multiple variants (X. M. Wang & Yue, 2006) in twinned coordination crystal structure through self-accommodation system (Otsuka & Ren, 2005). By applying a load, the structure transforms into the detwinned martensite phase at low transformation stress known as detwinning process (Hu et al., 2016). A large unrecovered strain is produced upon unloading that can only be returned by the application of heat at above its critical temperature. This transformation process explains the shape memory effect (Roubíček, 2005; G. Song et al., 2006).

Pseudoelasticity (PE) or superelasticity (SE) is the ability of an alloy to revert to its original shape after being deformed at a temperature between austenite finish temperature, A_f and the maximum temperature to observe pseudoelasticity before plastic deformation, M_d (L. McKlvey et al., 2000) without the need of any additional heat activation. The transformation involves the change of the austenite phase into a single-variant of the martensite phase. Since the austenite structure is stable at high temperature, higher critical stress is required to induce the martensitic transformation. Upon unloading, unstable martensite structure at high temperature instantaneously transforms back to the austenite phase. For temperature higher than M_d, shape memory alloy exhibits like elastic-plastic deformation of ordinary metal with the absent of martensitic transformation (Lobo et al., 2015).

Another unique behaviour of shape memory alloy is a two-way shape memory effect. The ability of the alloy to memorise its shape at both high and low temperatures. The behaviour requires shape training (loading-unloading) at the phase transition temperature of both austenite and martensite structures (Mohd Jani et al., 2014).

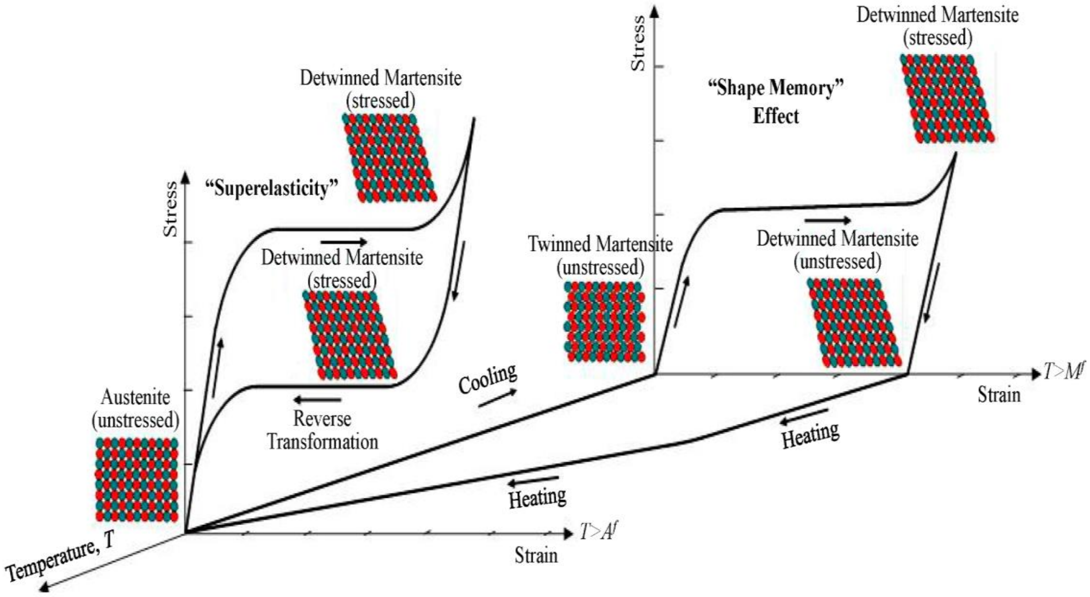

Figure 2.4. The behaviour of shape memory alloy based on phase transformations (Seo et al., 2015)

2.3 Nickel titanium (NiTi) shape memory alloy

The shape reversibility after the application of heat from the binary alloy of Ni-Ti sample was first observed at the Naval Ordnance Laboratory in 1959 (Honma, 1983). The discovery of the shape memory behaviour of NiTi alloy has boosted up the research on shape memory behaviour in another potential alloy. However, NiTi alloy is preferable for the commercialisation of shape memory alloy due to its stability in performing shape memory behaviour with good mechanical behaviour (Otsuka & Ren, 2005). Owing to strong corrosion resistance and excellent biocompatibility, NiTi has been applied widely in the medical field such as stents and orthodontic wire (Mohd Jani et al., 2014). Although NiTi alloy exhibits prominent stability of shape memory behaviour among all, the system is complex. The behaviour can be rapidly changed at different permissible compositions prior to thermomechanical treatment in manufacturing processes. The formation of impurities during heat treatment affects both the thermal and mechanical behaviour of NiTi alloy which can be understood by using a phase diagram (Otsuka & Ren, 2005).

2.3.1 Phase diagram of NiTi shape memory alloy

Figure 2.5 shows the phase diagram for NiTi shape memory alloy system. The diagram indicates a very tight atomic composition tolerance where the variation becomes wider as the temperature increases up to 1118°C and gradually decreases from that point. At a temperature below 630°C, NiTi phase only lies in one vertical line. This somehow susceptible for other impurities like Ni_4Ti_3 to appear simultaneously with the pure NiTi. The phase boundary for the Ti-rich side is almost vertical, indicating a narrow permissible solubility of titanium element. Exceeding the limit is likely to introduce Ti_2Ni precipitates into the matrix. In contrast, for the Ni-rich side, the solubility of Ni in NiTi increases as the temperature increases from 630°C and achieving maximum solubility up to 57at%Ni at 1118°C. The existing of excessive nickel in the matrix facilitate diffusional precipitation to form other phases including Ni_4Ti_3, Ni_3Ti_2 and Ni_3Ti through heat treatment.

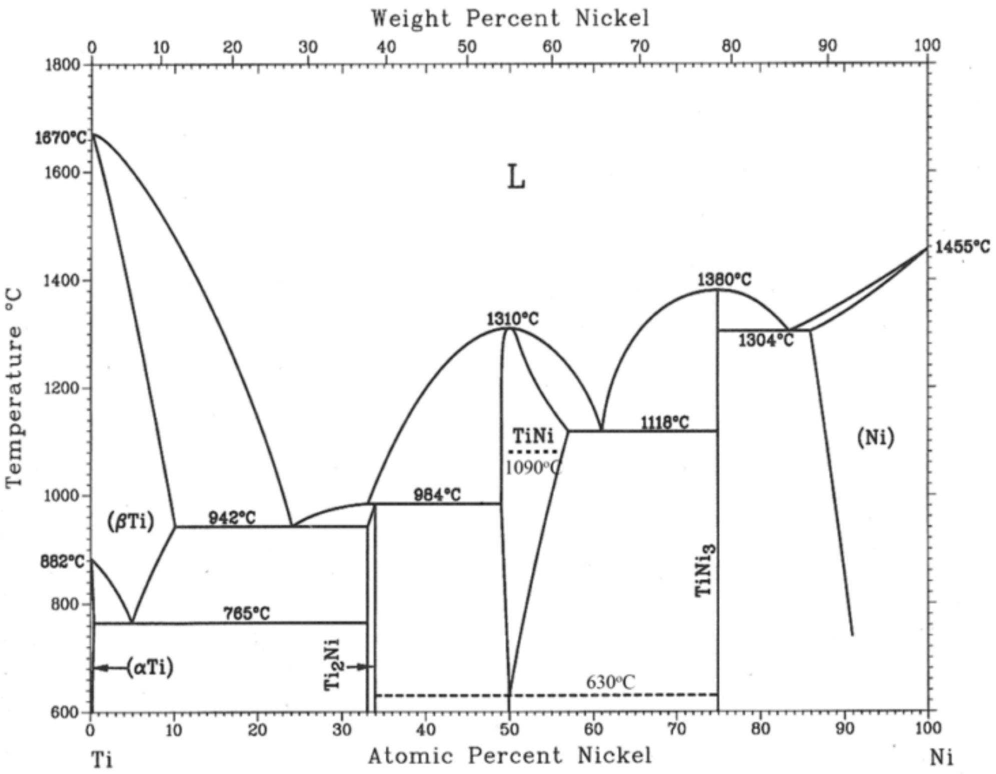

Figure 2.5. Phase diagram of NiTi alloy (K., Ren, et al., 1999)

2.3.2 The effect of NiTi composition on thermomechanical behaviour

NiTi shape memory alloy is very sensitive to alloy composition (Frenzel et al., 2015). The maximum solubility of Ni in NiTi is up to 57at%Ni at 1118°C. However, the concentration range of technical interest typically in between 49at%Ni to 52at%Ni to feature the shape memory behaviour (Gallardo Fuentes et al., 2002). Beyond the limit, no shape memory is accounted. Each composition has different corresponding thermomechanical behaviour associated with certain heat and thermomechanical treatment (Dlouhy et al., 2003). In most today practice, the addition of nickel element into the binary of NiTi has presented different martensitic transformation behaviour. As reported by J. Frenzel (Frenzel et al., 2010), the increase of Ni contents resulted in the reduction of the latent heat transformation and thermal hysteresis which subsequently caused the martensite start temperature (M_s) of solution treated NiTi to decrease by 10K for 0.1at%Ni is added as shown in Figure 2.6. By increasing the Ni content, the latent heat for austenite to martensite transformation decrease due to destabilisation and stabilisation of B19’ and B2 phases. It stabilises the B2 phase which therefore requires further cooling for martensite transformation. By having progressive compatibility in crystallography as Ni element is added to the stoichiometric NiTi, bring the geometry of B19’ phase closer to B2 and produce lower thermal hysteresis (Frenzel et al., 2015).

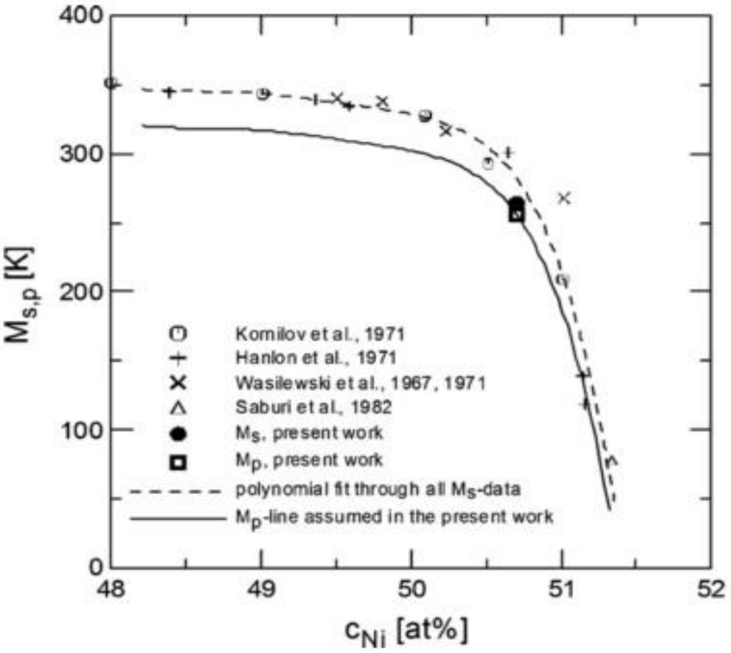

Figure 2.6. The correlation between Ni composition of NiTi and martensite start temperature (M_S) (Jafar Khalil-Allafi et al., 2009)

Previous studies have identified the relationship of Ni content and the shape memory behaviour. NiTi alloys with a composition close to 50.0at%Ni are more likely to behave one-way shape memory effect as the alloy can remember its original shape at high temperature. Meanwhile pseudoelasticity behaviour is more likely to be observed in higher Ni content of NiTi. Several conducted analyses revealed that the increase of Ni content within the matrix causes the phases transformation temperature to drop and it is convenient to observe pseudoelasticity at room temperature. In regard with this phenomenon, NiTi alloys with composition greater than 50.5at%Ni are classified as Ni-rich NiTi alloy (Mentz et al., 2008). Besides, prior to heat treatment, it was also investigated that the precipitation of producing the secondary phase change the alloy composition slightly. Generation of Ni_4Ti_3 for example, constantly disintegrate the nickel element in the matrix of pure NiTi for the composition to drop slightly (Ke et al., 2015).

2.3.3 Thermal transformation behaviour of NiTi alloy

Thermal transformation behaviour of shape memory is normally characterised from latent heat measurement made using differential scanning calorimetry (DSC). Single stage transformation is usually observed from a fully annealed NiTi as shown in Figure 2.7 (a). The curve represents the transformation sequence of austenite (A) to martensite (M) phase (A→M) transformation on cooling and martensite to austenite (M→A) on heating. Ageing at temperature 673 K, the curve in (b) shows the two-stage transformation. The transformation sequences involve two-phase transformations on cooling, austenite to R-phase, (A→R) and R-phase to martensite, (R→M) while M→A transformation on heating. By using partial cycle technique, the reverse transformation phase of R→A can be reproduced in the transformation window. The A↔R transition is an intermediate phase due to the occurrence of lattice distortion that causes the R-phase structure to exist (Y. Zhou et al., 2006). Thermal hysteresis and the latent heat of the M↔A transition is usually larger than A↔R transition.

Transformation curve in Figure 2.7(c) illustrates the effect of composition on the transformation behaviour. The aged sample of higher composition, Ti-50.5at%Ni represents the multi-step transformation on both cooling and heating. It also shows a larger thermal hysteresis of M↔A transition and very small thermal hysteresis of A↔R transition.

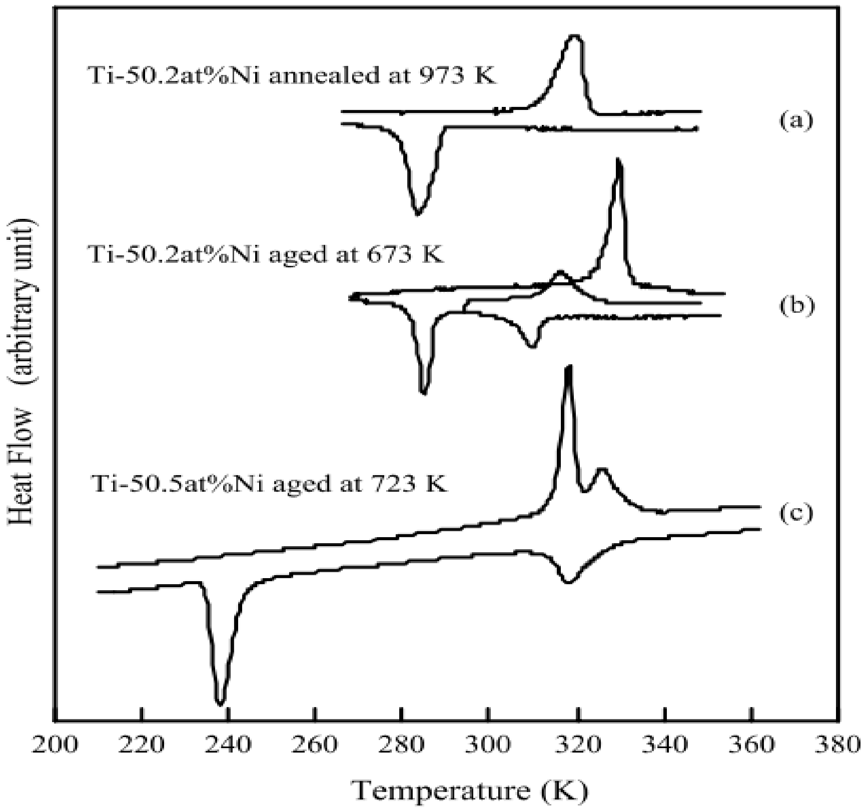

Figure 2.7. Transformation sequences in near-equiatomic NiTi alloys (Yinong Liu & McCormick, 1996)

2.3.4 Stress-induced martensite phase transformation behaviour of NiTi alloys

A stress-induced martensitic transformation produces macroscopic shape change. Figure 2.8 shows the typical martensitic transformation of the NiTi alloy as induced by stress under tensile loading. As the stress is applied, at some critical level of stress, (a), the parent phase of austenite becomes unstable and subsequently develops martensitic phase region. The transformation creates a percentage of strain (macroscopic elongation) with constant stress level. During the transformation (*a-b*), the two phases coexist, and the deformation is inhomogeneous until almost all the matrix is transformed into martensite phase as indicated by point (b). At (c), the austenite phase is fully transformed for detwinning process before slip at (d).

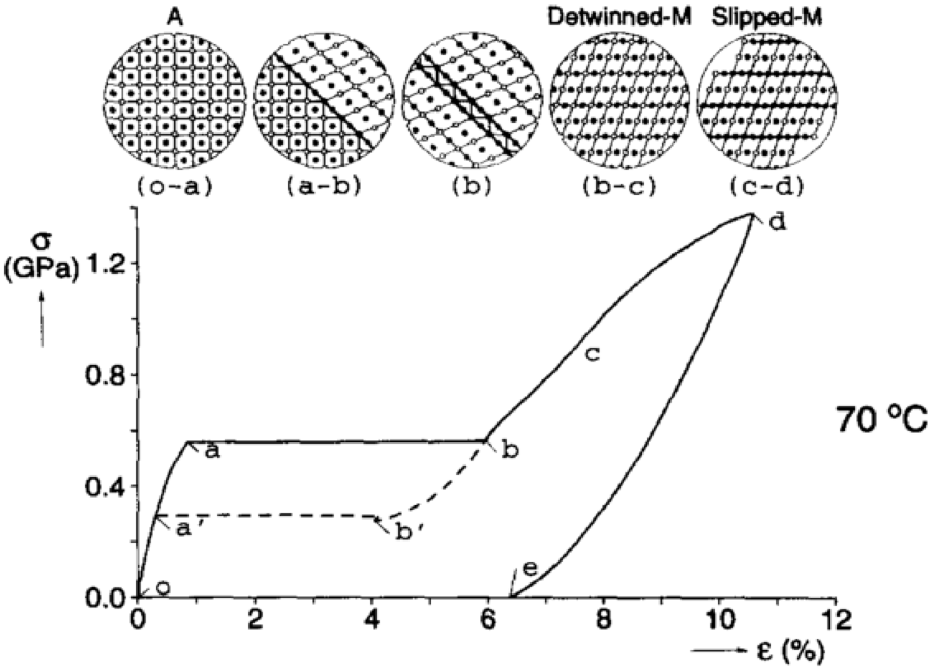

Figure 2.8. NiTi stress-strain curve of stress induced martensitic transformation and stress-induced plasticity at isothermal extension test at 70°C (Shaw & Kyriakides, 1995)

NiTi shape memory alloy is a temperature dependent alloy (Abel et al., 2004; Benafan et al., 2013). The operating temperature much influences the martensite transformation stress and pseudoelasticity. Figure 2.9 shows the proportionality of the critical stresses towards the operating temperature. The stress-induced martensite increases as the temperature increases. The temperature exceeding deformation temperature (M_d) would result in very high required transformation stress since the B2 phase gains higher stability (Lobo et al., 2015). Owing to low critical stress to slip causes the alloy to permanently deform and results in poor recovery. The environmental temperature somehow limits the applicability of the NiTi alloy. The drawback is pseudoelasticity could not be well performed at large temperature range. At lower temperature may cause insufficient input thermal energy for recovery while at the higher temperature results in slip deformation.

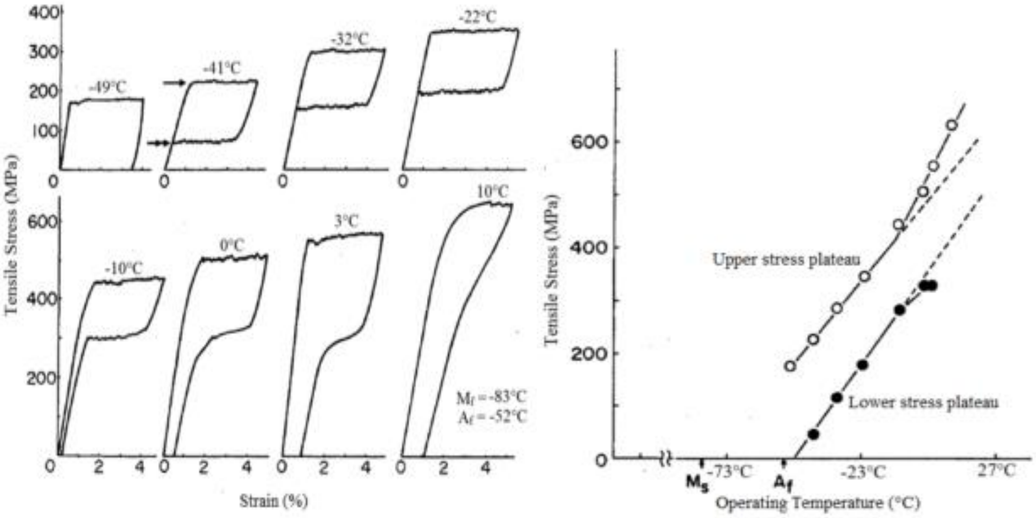

Figure 2.9. The effect of operating temperature on critical stress to induced transformation and pseudoelasticity (Otsuka & Ren, 2005)

Figure 2.10 shows the effect of deformation strain rates on the stress-induced martensite. The transformation stress increases as the strain rate increases (Zhang et al., 2018). In the time of deformation, heat is eventually released due to a different direction of atomic movements and elevates the temperature at the vicinity of the untransformed region. This phenomenon is known as self-heating of NiTi alloy. At high temperature, the B2 phase becomes more stable and consequently requires higher stress to induce the transformation. It has been proposed that the self-heating effect could be eliminated or minimised at slower deformation strain rate of $0.0167 s^{-1}$. It is also found that pseudoelasticity is less affected by strain rate as shown in figure 2.10.

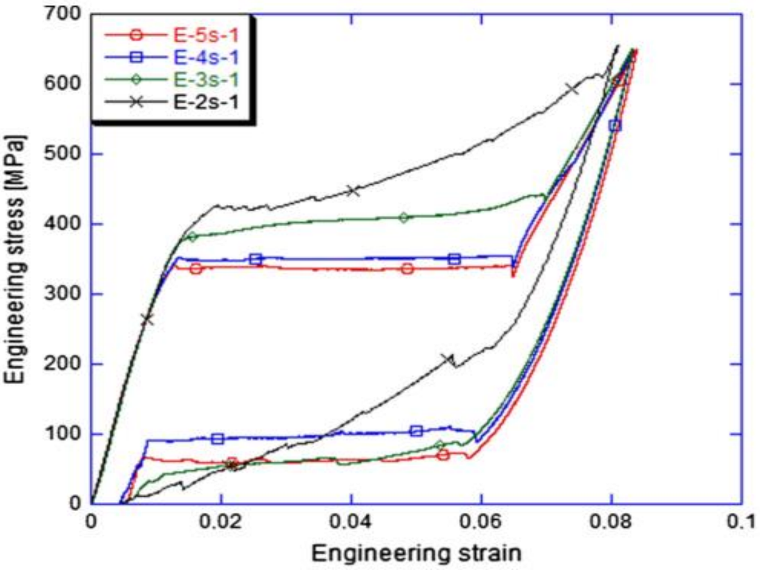

Figure 2.10. Stress–strain curves of the NiTi alloy at different strain rates (Gamaoun & Hassine, 2014)

2.3.5 Thermomechanical treatment on NiTi shape memory alloy

Theoretically, shape memory effect and pseudoelasticity are expected to exhibit complete strain recovery upon reverse phase transformation. However, due to low yield stress induces dislocation during transformation leaving a permanent strain. The inelastic behaviour is also caused by insufficient of heat to drive back the deformation to the original state. The irreversible transformation somehow confines the durability and applicability of the NiTi alloy when subjected to multiple transformations (Sehitoglu et al., 2000). Several thermomechanical treatments are required to achieve higher critical stress for the slip. Increasing the slip stress extends the workability of NiTi alloy at a wider temperature range. Two prominent methods have been practically used are work-hardening and aged or precipitation hardening.

Work-hardening introduces lattice defects with high dislocations density within the microstructure. It increases the critical stress for slip through propagation and nucleation of diffusionless transformation that affected by existing dislocations

(Treppmann & Hornbogen, 1997). Work-hardening is usually applied on NiTi alloy with Ni content of 49.5at%-50.5at%. The high density of dislocations is induced through cold work with followed by annealing below crystallisation temperature. Annealing at a temperature above crystallisation temperature contributes no hardening effect. No ageing effect is observed after heat treatment because of low Ni content. Cold-drawn and annealed wires have successfully improved the pseudoelasticity and shape memory effect as compared to solution treated condition (Ken Gall et al., 2008).

In contrast, precipitation or age hardening is inducing a secondary phase into the matrix which acts as a hardening agent through ageing treatment. Age-hardening is usually applied to Ni-rich NiTi alloy. The presence of excess Ni facilitate the precipitation to produce Ni-rich precipitates of Ni_4Ti_3. Ageing treatment is time and temperature dependent heat treatment. It was found that only high density of coherent precipitates would effectively raise the flow stress to slip. It is only can be achieved through a proper combination of temperature and time. Over-ageing always comes out with larger and low density of precipitates thus ageing becomes less effective to enhance the shape memory and pseudoelasticity.

It was found that the combined effect of cold-working and ageing have given a significant effect on the critical stress for the slip. Figure 2.11 shows the combination of the hardening effects of Ti-50.6at%Ni towards transformation stress and pseudoelasticity. From the figure, complete recovery is observed at deformation temperature of 313 K and above. Accompanied with high transformation stress also indicates better stability for a wide range of applicability of NiTi, especially in cyclic deformation applications.

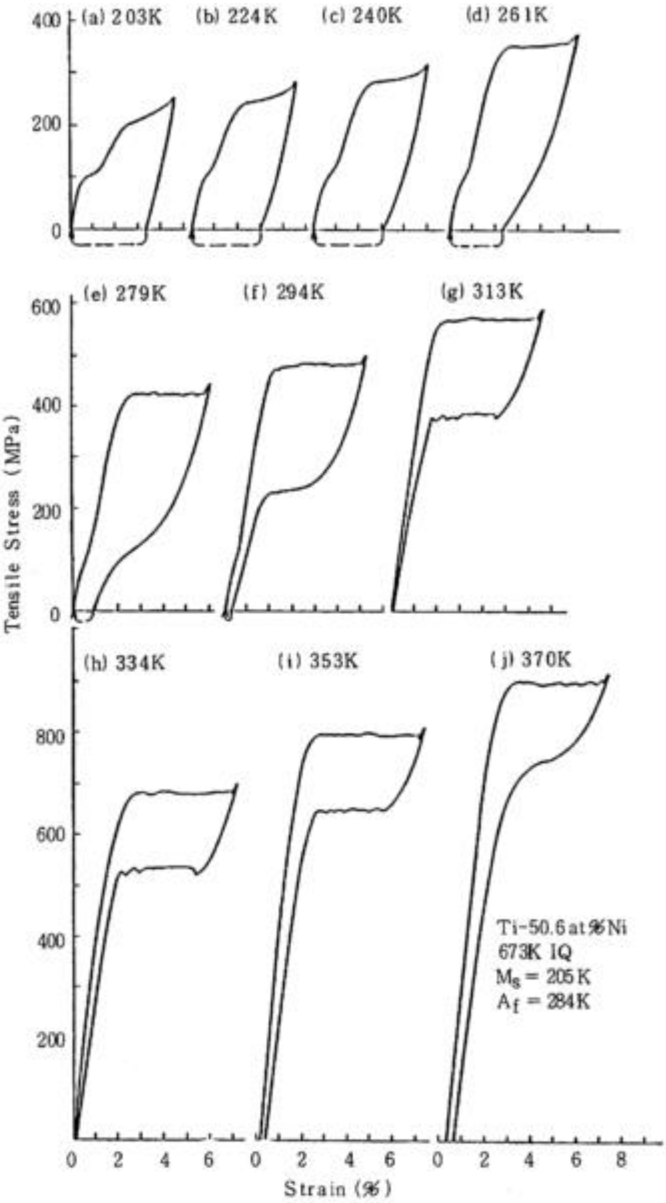

Figure 2.11. The combined effect of ageing and annealing on the deformation behaviour of Ti-50.6at%Ni (Otsuka & Ren, 2005)

2.4 Effect of ageing on shape memory behaviour of NiTi alloys

Ageing is a temperature and time-dependent heat treatment for NiTi alloy. It is seen to be less effective for NiTi alloy of <50.6at%Ni, but its influence is prominent for alloy with Ni content above 50.8at% (Miyazaki et al., 1982; Y Liu & Galvin, 1997). Effect of ageing towards NiTi shape memory alloy system is very complex. It requires only the coherent Ni_4Ti_3 precipitate to influence its behaviour, thus under-ageing or over-ageing do not contribute to the shape memory behaviour. Additionally, the shape memory behaviour is also influenced by the homogeneity and heterogeneity of the precipitates in the matrix.

2.4.1 Effect of ageing on transformation behaviour

Martensitic transformation of NiTi alloy is responsive to the change of the lattice structure, and so for ageing treatment, that modifies the microstructures through the production of metastable phase precipitates. There are three common phases exist in the transformation of aged NiTi alloy, B2 phase referred as austenite (A), B19' phase which is martensite phase (M) and R-phase which is a rhombohedral phase (R). The transformations involve the lattice distortion of microstructure involving A ↔ M, A ↔ R and R ↔ M transformation.

Ageing usually accompanied with prior solution treatment at the temperature typically 900°C. Figure 2.12(a) shows single-stage transformation, B2 ↔ $B19'$ for the solution treated of NiTi alloy on cooling and heating (F. Jiang et al., 2009). It is well known the presence of Ni_4Ti_3 responsible for the formation of R-phase in the transformation window after ageing as shown in the figure 2.18(b) (Kim et al., 2004). At initial ageing stage, the $B2 \rightarrow R$ transformation usually appears at higher temperature with small latent heat. At the same time, higher transformation resistance generated by fine precipitates, shift the $R \rightarrow B19'$ to lower transformation temperature. It is also reported in some literatures (Genlian Fan et al., 2004; Karimzadeh et al., 2016), higher Ni-content of NiTi induce high density and finely dispersed Ni_4Ti_3 that suppressed $R \rightarrow B19'$ transformation on cooling.