

DESIGN AND FABRICATION OF SHAPE MEMORY DEVICE

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Declaration

I declare that the work in this dissertation was varied out in accordance with the requirements of the University's Regulations. This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree. This thesis is the result of my own investigations, except where otherwise stated. Work done in collaboration with, or with the assistance of others, is indicated as such. I have identified all material in this dissertation which is not my own work through appropriate and explicit referencing and acknowledgement. Where I have quoted from the work of others. I have included the source in the references/bibliography. Any views expressed in the dissertation are those other author. I hereby give consent for my thesis, if accepted, to be available for photocopying and for interlibrary loan, and for the title and summary to be made available outside organizations.

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List of Abbreviations

1. A	Austenite
2. A _s	Austenite start temperature
3. A _f	Austenite finish temperature
4. M	Martensite
5. M _d	Martensite deformation limit temperature
6. M _f	Martensite finish temperature
7. M _s	Martensite start temperature
8. Ni	Nickel
9. Nitinol	Nickel-Titanium
10. R-phase	Rhombohedral-phase / trigonal martensite phase
11. RE	Residual elongation
12. Ti	Titanium
13. SME	Shape memory effect
14. SMA	Shape memory alloy
15. TWSME	Two ways shape memory effect
16. OWSME	One way shape memory effect
17. PE	Pseudoelastic
18. B2	The structure of the parent phase in Ti–Ni based alloys
19. B19'	Monoclinic martensite structure
20. SIM	Stress induced martensitic
21. DSC	Differential scanning calotimeter
22. TTR	Transition temperature ranges

Abstrak

Aloi memori bentuk (SMA) telah dianggap sebagai salah satu bahan pintar dan mampu menjanjikan keberkesanan dalam penerapan teknologi . Terdapat banyak penggunaan bahan pintar ini yang telah diimplementasi untuk dilaksanakan pada pelbagai aplikasi seperti penggerak, aplikasi bioperubatan dan sebagainya. Aloi memori bentuk mempamerkan keupayaan unik di mana bahan ini memulihkan bentuk asalnya apabila sudah berlaku transformasi pada bentuknya melalui fasa thermo-elastik yang mampu diterbalikkan, membolehkan bentuk aloi memori untuk memulihkan pemanjangan yang besar yang boleh mencapai 8% yang sudah mencapai nilai yang cukup besar, sama ada secara spontan iaitu pseudokekenyalan atau melalui peningkatan suhu iaitu kesan memori bentuk. Jika diperlihatkan dalam kalangan aloi memori bentuk yang sudah berada di pasaran, nikel-titanium merupakan aloi yang luar biasa kerana prestasi dan kebolehpercayaan bahan ini dalam implementasi.

Kajian dilakukan untuk memperlihatkan aloi memori bentuk dua hala yang boleh diaplikasikan. Kajian yang dilakukan adalah untuk mereka dan membangunkan sebuah alat dengan menggunakan kesan bentuk memori. Kajian ini adalah dengan menggunakan gabungan kedua-dua latihan iaitu bentuk memori dan pseudokekenyalan. Kaedah yang digunakan adalah untuk memperoleh perubahan pada bentuk asli ketika panas bersama-sama dengan suhu transformasi selepas proses latihan, dan hasil yang berkesan bagi bentuk ketika sejuk. Bentuk yang ditetapkan ialah lengkungan dengan 90° dari pusat dan wayar sepanjang 10cm untuk setiap sampel bagi menggambarkan pergerakan kelopak bunga. Eksperimen dikendalikan adalah tanpa kehadiran fasa R dan adanya fasa R dalam kawat Nitinol digunakan. Hal ini kerana bahawa tanpa wujudnya fasa R merupakan cara terbaik untuk menunjukkan peningkatan julat nilai martensit. Selain itu, penggunaan Nitinol adalah untuk pelaksanaan dalam reka bentuk untuk mencapai bentuk aloi memori dua hala yang memberikan tindak balas terhadap perubahan suhu sekitar. Dengan ini, aloi memori bentuk yang digunakan berupaya mencapai kesan bentuk memori dua hala yang mengingati bentuk bagi kedua-dua fasa iaitu martensit dan austenit.

Abstract

Shape Memory Alloys (SMAs) have been considered as one of the most promising smart and advance materials. A lot of idea generated on using this advance material for implementation into various applications such as actuator, biomedical application and etc. Shape Memory Alloys demonstrate a unique ability to recover their original shape after deformation through a reversible thermo-elastic phase transformation, it allows shape memory alloys to recover large strains which can reach 8% the most. Among the commercially available shape memory alloys, nickel–titanium ones are outstanding due to their excellent performance and reliability.

A case study approached was employed to demonstrate the workable two-way shape memory alloy. This study is aiming on the design and development of tool by utilizing the two-way shape memory effect. The idea is to combine both shape memory and pseudoelastic training. This method is to gain changes in the original hot shape together with the transformation temperatures after the training process, and the effective outcome of the cold shape. The shape set is an arc of 90° with 10cm length to for each of the sample to illustrate the movement of flower petal. The experiment of dealing the Nitinol wire with and without the presence of R-phase as it is the best realise that by supressing the R-phase able to increase the range of martensite values. Furthermore, the training method used for Nitinol wire to exhibit the two-way shape memory effect that gives respond towards the change of surrounding temperature. Thus, the NiTi shape memory alloy able to develop the two-way shape memory effect to perform the shape set for both martensite and austenite phase.

Chapter One: Introduction

1.1 Nickel titanium shape memory alloys

Shape memory effect has been first discovered in 1932 by L.C Chang and T.A Reas on a gold-cadmium alloy. This effect has then been observed in 1938 on a copper-zinc alloy but the extended research into application was not conducted until 1962. The Nitinol alloy became popular after the discovery as it was first developed at the Naval Ordnance Laboratory in White Oak, Maryland and commercialized under the trade name Nitinol. Basically, Nitinol belongs to a class of materials called shape memory alloys that can sustain large amounts of plastic deformation and has an elastic limit of on average 1–8% strain. Shape memory alloy exhibit shape memory effect as it able to add the anthropomorphic qualities of memory and trainability.[1]

Besides, if such alloy is plastically deformed at one temperature, it will completely recover the original shape on being elevated to a higher temperature. In recovering its shape the shape memory alloy can produce a displacement or a force as a function of temperature. This change is reversible and can be repeated many times.[2] Exploration of advanced SMAs with both low stress hysteresis and large pseudoelastic strain is of significant for practical applications. For most materials, if they are bent out of shape, they will stay that way. However, in normal metals, deformations causes the dislocations of the molecular structure into new crystal positions. There is no "memory" in the crystal of where the atoms were before they moved.

Furthermore, from figure 1 as the martensitic transition is initiated when the alloy passes through a critical temperature during cooling called M_s (martensite start) and is completed at M_f (martensite finish). Plus, when the material is totally martensitic, it will loses its structure and shape and achieves maximum flexibility. [3] While when the temperature is elevated, the martensitic transition in austenite is initiated at temperature A_s (Austenite start) and finalized at A_f (Austenite finish), when the Nitinol alloy is totally austenitic, recovering its shape and achieving maximum rigidity. As a response to the temperature variation, the crystalline structure presents deformations in the molecular

arrangement, without changing the atomic composition. Most solids exhibit just one crystalline structure whereas Nitinol has two. The change from one structure to the other is a real solid-solid phase transition, similar in many aspects to the more usual solid-liquid transition. The transition between the two phases is in fact likewise induced by a change in temperature, the applied force, or a mix of the two factors.[4]

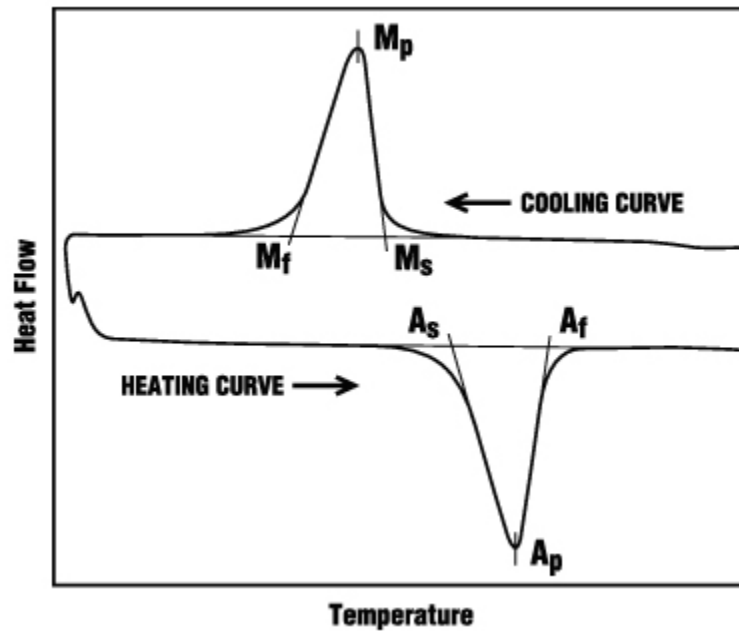


Figure 1. A DSC curve for a NiTi Shape Memory Alloy.

The distinctive mark of any phase transition is the sudden change in one or more physical properties. The macroscopic properties of a material in fact strongly depend on the crystal lattice structure, thus explaining why even a slight change in atoms arrangement can result in materials exhibiting quite different properties.

To perform the responds toward temperature change, there are two particular type of shape memory effect which is one way and two-way shape memory effect. There are several ways of training a two-way shape memory effect which is by combining shape memory and pseudoelastic cycling training. This can be done by heating the specimen above A_f and M_d (highest temperature at which martensite formation can be induced by stress) where pseudoelastic behaviour is expected which then load it in austenite state to a

desired cold shape. This proceed with cooling it in the loaded condition below M_f and then unload the specimen completely.

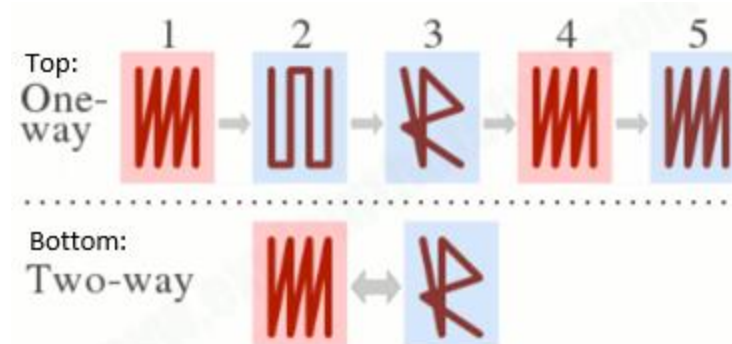


Figure 2. One way shape memory effect and two-way shape memory effect.[5]

Comparing shape-memory effects.

Top: The one-way shape-memory effect.

- 1) The wire is programmed by bending it into a specific shape at a high temperature.
- 2) Once it's cooled down, the wire can be bend into a different form.
- 3) The wire can be bend into any number of other shapes.
- 4) When the wire is heated above a critical temperature, it automatically springs back to its originally remembered shape.
- 5) If the wire is cooled down, it stays in that shape.

Bottom: The two-way shape-memory effect.

The material exists in one shape above a critical temperature and in a different shape below it. It flips back and forth between these two shapes as the temperature changes.[5]

1.2 Problem Statements

Nitinol is not an ordinary material that behave like most alloy as it have the ability to transform its shape for other useful purpose. A lot of application that work with this kind of smart material are not widely known as this is a kind of huge investment research to deal with. Nitinol can be apply as a device that giving respond towards surrounding temperature. This is due to the attribute which is recognised as the shape memory effect and pseudoelastic. Furthermore, Domestic purpose device with common material cannot respond towards environmental change to be function. This is a limiting factor due to the material which have limited flexibility quality. For a device to perform a certain task with natural way of initiator is quite impossible for a regular material. The idea of moving a certain part of the device with temperature stimulation is one sort of understanding that need to be concern.

Besides, the used of Nitinol in the application is not an easy task. The material have specific composition which allow it to express the optimum two-way shape memory effect. So, in gaining the desired shape there is some certain consideration that need to be include like the training method and characteristic temperature. In term of training, there were many type of training that have been highlighted for getting the desired outcome that can present the shape memory effect specifically the two-way shape memory effect. Two-way shape memory effect is a behaviour that can be used to exhibit the phase transformation for both the martensite and austenite. Most of the reported studies on shape memory effect are focusing more on the implementation of NiTi alloy in actuator and biomedical field like the orthodontic.

1.3 Objectives

- a) To design and develop a small device utilizing two-way shape memory behavior of NiTi SMA.

1.4 Scope of the project

The work that will be completed is focusing on the development and design of small device utilizing two-way shape memory behaviour. The application of a shape memory device. The major accent is basically on the design configuration for domestic use by first understand and analyse the foundation of the shape memory alloy. Next, the best method of training is needed to get the desired shape of Nitinol specimen to give a more efficient motion that lead to responsive action when undergoes temperature change. . In getting the final workable device, the vital part to be understand is considering all the parameters like the precipitation, R-phase and other properties which contribute to the material responds toward surrounding change and the training outcome. Thus, this work scope involves the use of shape memory alloy with exhibiting the two-way shape memory behaviour.

Chapter Two: Literature review

Generally, there are a lot of study have been done regarding the Nitinol as it is a smart material that give a large shape memory effect. Many researches of application detail analysis are been focusing as the implementation of the material for further develop is one great work of achievement. The researchers are exploring more into the material development and application which in biomedical field like the orthodontic and the actuator applications. The advantage of this Nitinol based research is the behaviour like the shape memory effect and pseudoelastic which both are the focus of the most study for applying and experiment purposes. However, the visualize idea is the two-way shape memory effect which giving two-way shape memory effect when cooling–heating or heating-cooling cycle.

Besides, there is also unavailable in the market which means to have a completed structure is hard to have it. The manufacturer is active regarding the Nitinol just as the provider of the material in various shape with specific ratio of components which is a good opportunity to start a research from a readymade film or wire shape of Nitinol.

Furthermore, to gather the useful information to apply in this project and proof that it is possible to train a shape memory alloy into the desired shape, a wide perspective of view is needed to have a focus scope of research towards the end.

2.1 Nitinol's Crystalline Structure

The properties of Nitinol depend upon its dynamic heat sensitive crystalline structure. When cooled, low temperature martensite is formed whereas the elevation of temperature cause the formation of austenite. Martensitic phase is a low temperature phase. The crystal structure is aligned and cubic. The alloy may be bent or formed easily. While austenite phase happen when the temperature is above transition temperature. Besides, the annealing phase is the high temperature phase. The alloy will reorient its (cubic) crystalline structure to "remember" its present shape.[6]

2.1.1 Nitinol exhibits two crystal forms:

Austenite: this is a phase where it is stable at high temperature. The lattice shows a body centered cubic symmetry (BCC) with B2 symmetry, which means that atoms occupy the vertexes of two intertwined primitive cubic lattices. In this form Nitinol is very stiff and not easily deformed.

Martensite: this is a phase where it is stable at low temperature. The crystalline structure is a stretched monoclinic and has B19 symmetry, exhibiting far less symmetry than BCC. Nitinol is now highly pliable and can be easily bent, but such a deformation is not permanent. Actually this phase initially comes in twinned mode (this means that it exhibits a mirror symmetry, with an ideal symmetry plane in between two cells, without the creation of any permanent defects in the crystal lattice). The twinned structure can be easily deformed, stretching out into the detwinned form like a folding hood. This process is reversible precisely because the sliding of the crystal planes did not create any defect. In the martensitic phase. The material can endure a huge deformation due to high mechanical stress still without any break in chemical bonds.[4]

If temperature drops below a specific temperature and neither load nor pressure is applied, the material transitions from austenite into twinned martensite. Reversely on heating, the material undergoes the inverse transformation. This phase transition does not

exhibit the usual “step “at specific temperature, namely the characteristic temperature, of traditional phase transitions. Nor does any isothermal transformation take place during which the absorbed/emitted heat is employed to transform a certain quantity of the substance from one phase to the other, as it happens for instance when water freezes into ice. Actually the austenite-twinned martensite transition is completed only when all domains have been transformed into the twinned phase, and this happens with continuity through a whole range of temperatures, starting at a specific temperature M_s and ending when M_f is reached. Below M_f , domains will be 100% martensite and the transition is fully accomplished.[4]

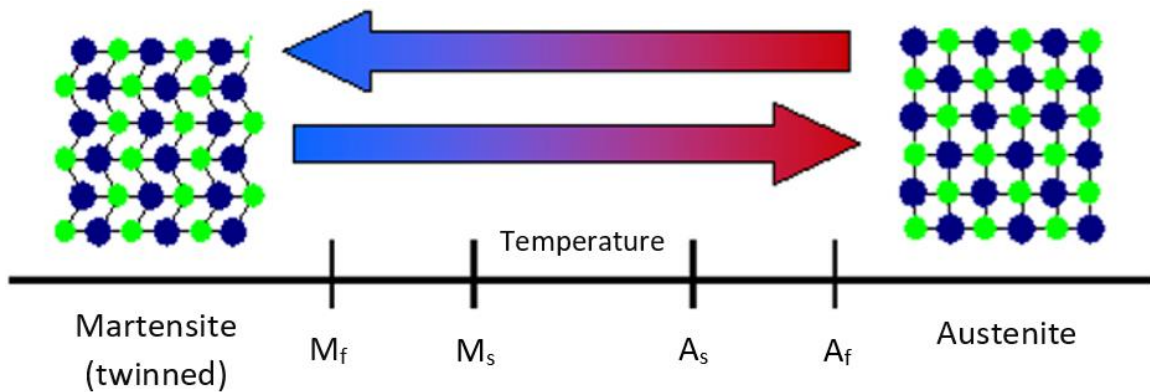


Figure 3. The illustration of crystalline structures in responding to the specific critical temperature.[4]

Table 1. Characteristic temperatures

Characteristic temperature	Description
M_s	Martensite start. It's the temperature starting the transformation process from austenite to martensite.
M_f	Martensite finish. At such temperature the transformation process from austenite to martensite is completed.
A_s	Austenite start. It's the temperature starting the inverse transformation process from martensite to austenite.
A_f	Austenite Finish. At this temperature the transformation process from martensite to austenite is completed.

2.2 Springback effect

Springback is basically the maximum elastic deflection that a specimen can stored in it. This is a measure of how far a specimen can deflected without causing permanent deformation. Nitinol wires have greater springback and larger recoverable energy than stainless steel. The first important factor has to do with displacement of molecules within the material, and the second has to do with stress and strain. When the specimen is bent, the outer region is stretched while the inner region of the bend is compressed, so the molecular density is lower on the outer surface than on the inside of the bend which can be seen in figure 4. The compressive forces are less than the tensile forces on the outside of the bend, and this causes the material to try to return to its original position. Nitinol have high springback effect.[16,17] . Spring back is more obvious in elastic deformation but in SMA the deformation is martensite phase transformation which have been stated in previous section. Also, the phase transformation is expected to be able to deflect and transform it shape like in figure 6.

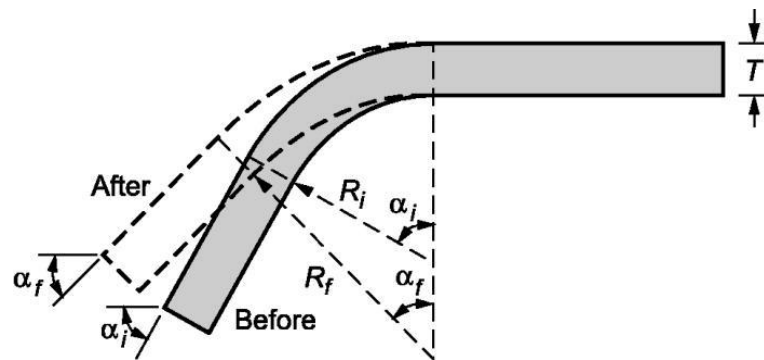


Figure 4. the illustration of bending on the shape memory alloy.[7]

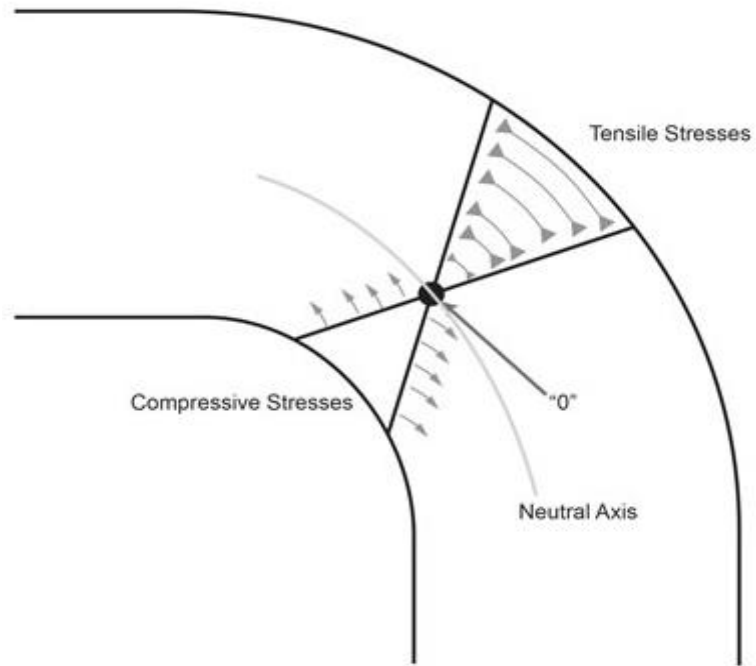


Figure 5. Compressive and tensile stresses exerted in shape memory alloy.[8]

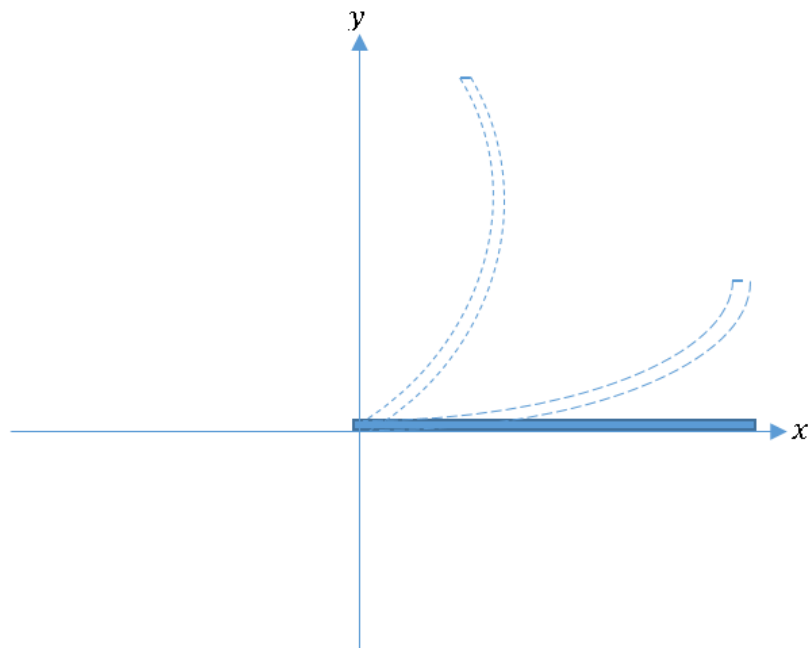


Figure 6. Deflection due to martensite phase transformation.

2.3 Superelastic and shape memory effect properties of Nitinol

Superelasticity is a unique property of SMA. If deformed at a temperature which is slightly above their transformation temperatures, it springs right back into shape. This springy property is called superelasticity. Whereas the shape memory effect is when a shape memory alloy is in its martensitic form, it is easily deformed to a new shape. However, when the alloy is heated through its transformation temperatures, it reverts to austenite and recovers its previous shape with great force. This process is known as Shape Memory.

The basic requirements for shape memory effect as well as superelasticity. Otsuka and Shimizu once proposed three requirements for effects which are thermoelastic nature of the transformation, ordering, and twinning as a deformation mode. The thermoelastic transformation is characterized by the mobile boundary between parent and martensite, and a small temperature hysteresis, which indicates a small driving force for the forward or reverse transformation, and thus indicating negligible possibility of introducing irreversible process such as slip. The transformation usually is also associated with the crystallographic reversibility, leaving any macroscopic debris on the surface after the reverse transformation. If stress is applied to a shape memory alloy in the temperature range above A_f , martensite can be stress-induced. Less energy is needed to stress-induce and deform martensite than to deform the austenite by conventional mechanisms. Up to 8% strain can be accommodated by this process. As austenite is the stable phase at this temperature under no-load conditions, the material springback into its original shape when the stress is no longer applied. This elasticity is also called pseudoelasticity or transformational superelasticity.

Since mobile boundary upon changing temperature or stress is necessary for superelasticity and the shape memory effect, which occurs at a temperature above A_s , thermoelastic nature is a required condition for the shape memory effect/superelasticity. Twinning as a deformation mode is also a necessary condition, because slip is an irreversible process. Besides, the characteristic of the twinning in martensite, which is equivalent to the change of correspondence variant. This promotes the strain attained by twinning or detwinning of martensite to recover upon the reverse transformation. The

condition, that twinning or detwinning is equivalent to the change of correspondence variant which is usually met. This is because twins introduced as a lattice invariant shear have this characteristic, and there are such twinning modes with small twinning shears.

For instance, low temperature nitinol wire is used as orthodontic archwires in braces. [9] The nitinol wire provides a low constant force at human body temperature used to straighten teeth while reducing the need for wire retightening. The transition temperature of these wires are made so that they generate force at the temperature of the human mouth (about 37C (98.6F)). Superelastic nitinol tubing is used as surgical catheters. The Nitinol catheters can be bent more often than their steel counterparts allowing surgeons to access difficult areas of the human body.

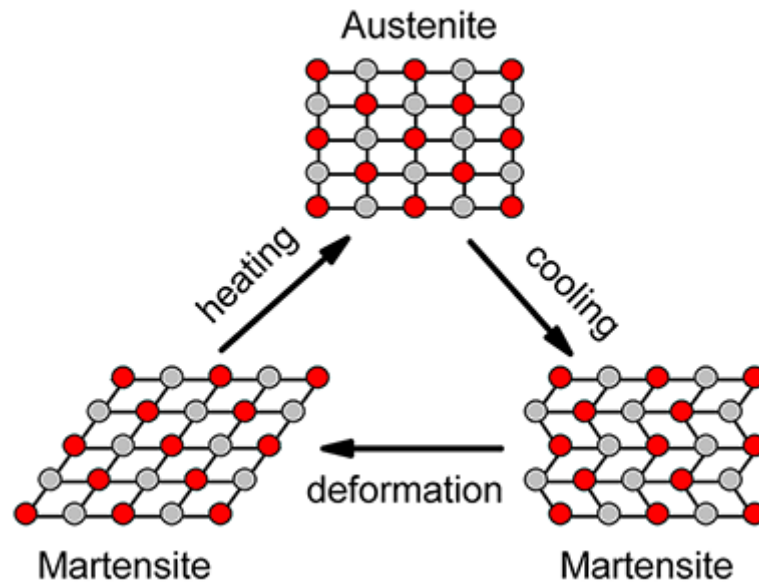


Figure 7. Microstructure variation during shape memory effect.[10]

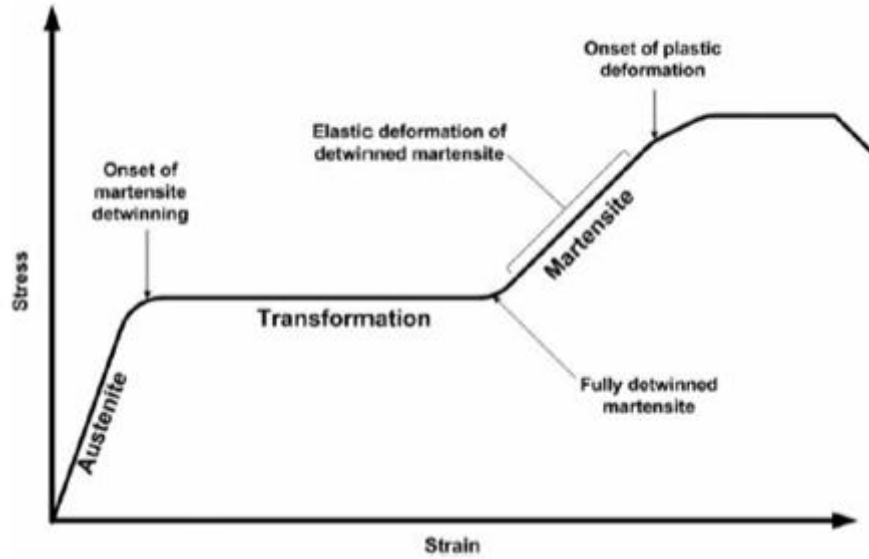


Figure 8. Phase transformation during superelastic effect.[10]

2.4 Two-way shape memory effect

The mechanism of SME only the shape of the austenitic phase is remembered. However, it is possible to remember the shape of the martensitic phase under certain condition. This behavior is a common property of SMA, it is called two-way shape memory effect (TWSME), it is known that the TWSME can be induced in single crystals by training, this means that dislocations acquire a convenient distribution to trigger the shape transformation in some prescribed way, after the removal of the external stress. It is also possible to consider the case of a sample that is engineered with a collection of dislocations distributed in some appropriate manner, such that the sample may have a tendency to spontaneously elongate in one direction and contract in the perpendicular one upon the martensitic transformation. Although at present it is not feasible to produce such an ad hoc distribution of dislocations, this seems an interesting theoretical situation to consider.

Shape memory alloy possess the shape memory effect which is reversible which can be recognized as two-way shape memory effect (TWSME). Besides, Nitinol is exhibiting the two-way shape memory effect (TWSME) which occurs due to the change in the crystalline structure of materials. The TWSME represents reversible way through a

hysteretic loop in the strain temperature response. This is the consequence of reversible phase transformations observed without application of any external force. This provides local stress and favours the formation of a preferred orientation to a net shape variation. However, the TWSME is not an inherent property of SMAs, but can only be obtained through a suitable thermo-mechanical treatment, usually termed training. [10,11]

In particular, there are three key microstructural forms for SMA. The first is austenite, the second is martensite. The third is a stress-biased martensite, is created either by stressing martensite below M_f , or by stressing austenite near but above A_f . The process of martensite reorientation proceeded through a localized manner over a distinct stress plateau and continued into the next stage of uniform deformation with an increasing stress. The martensite reorientation process is the transition from a localized manner to a uniform manner during tensile deformation of a polycrystalline matrix.

Deformation by martensite reorientation causes a thermal stabilization effect on the reoriented martensite. This stabilization effect is attributed to variations in the internal elastic energy and irreversible energy that accompany the transformation. Martensite reorientation deformation is effective in term of introducing a two-way memory effect. The magnitude of the two-way memory effect induced by simple tensile deformation of martensite is comparable to the two-way shape memory effect.

2.5 NiTi memory training

A common practice for not only stabilizing the shape memory behavior of various materials but also for inducing TWSME is known as 'training'. Training is a thermomechanical treatment involving repeated thermal/stress cycling, which is performed until the shape memory properties like the transformation temperatures, recovery strain, thermal or stress hysteresis are stabilized. Increasing the stress or strain levels during thermal or deformation cycling often leads to a higher concentration of defects, increasing the resulting TWSME.

Smart metals are not only able to remember their original shape, but they can also be trained into memorizing a new one. Nickel and Titanium atoms inside any of the many crystal domains called “grains” are almost perfectly aligned. Although, as usual in many crystals, a few defects, called dislocations, may occur. Dislocations originate from the sliding of a lattice plane induced for instance by huge mechanical stress and bringing to deformation. Actually this deformation is possible only because of the presence of dislocations. Arising of dislocations implies that chemical bonds have been broken. Therefore to produce such defects quite a lot of energy is needed and once they have been produced they are indeed quite stable.

Even if the percentage of this kind of defects is very low if compared to the total number of atomic planes in the crystal, they represent, together with grain borders and precipitates, the main cause for Austenite shape memory properties since they “pin” its macroscopic shape. Such defects are in fact energetically stable and they do not change according to phase variation since, such transformations take place with no break and rearrangement of chemical bonds. This is why in martensitic phase upon moderate heating the metal goes back to its original shape, characterized by a specific defect configuration in the austenitic phase.

List of four main training methods for NiTi TWSMA:

(a) Shape memory (SME) cycling (Cool-Deform-Heat):

Cool the alloy below M_f , deform below shape memory strain limit, heat to recover the parent phase shape and repeat this cycle for 5-10 times, the specimen begins to spontaneously change shape on cooling to trained, deformed geometry.

(b) Constrained cycling of deformed martensite:

Cool the alloy below M_f and bend (or deform) it severely beyond the shape memory recoverable strain limit. When the specimen is heated above A_f , the material will not recover the original shape completely, however, if cooled below M_f again, the component moves partly toward the over-deformed shape.

The deformation to the trained shape in full martensite (in methods (a) and (b)) originates from the reorientation of martensite, a process in which the resulting dislocation arrangements bring about a large permanent strain that will affect the hot shape.

(c) Pseudoelastic (PE) cycling (Load-Unload):

Repeatedly load and unload the austenite phase at a temperature above A_f , but below M_d . In this method, loading and unloading occur in full austenite which is difficult to introduce the memory. This is due to the high level of stability of the austenite phase, so the amount of dislocation arrangements produced is too small to remind the trained sample of the cold shape.

(d) Combined SME and PE cycling:

Combining (b) and (c) above has been shown to be a very effective training schedule. It consists in deforming the parent austenite by introducing stress induced martensitic (SIM), followed by a cooling cycle below M_f at constant strain induced in the sample. Subsequently, the specimen is heated to recover the original shape and this cycle is repeated a few times until TWSM behaviour is manifested in the material upon cooling and heating. Method (d) results from the loading that takes place in full martensite and the effective dislocation arrangements that give rise to the formation of the cold shape upon cooling with little influence on the recovery of the hot shape upon heating.

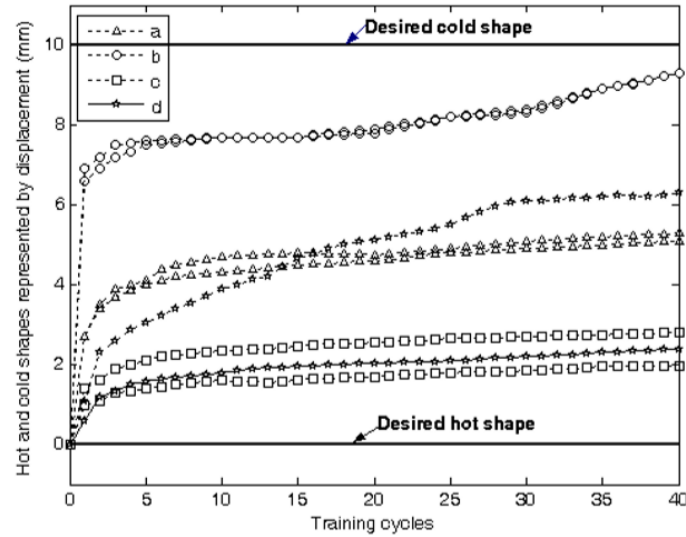


Figure 9. Comparison of hot and cold shapes versus training cycles for the four training methods.[13]

By comparing the hot shape curve and the cold shape curve for each training method, it can be seen that only the specimen trained by method (d) shows a significant difference between its hot shape and cold shape, while those trained by the other three methods exhibit a similar hot shape and cold shape.

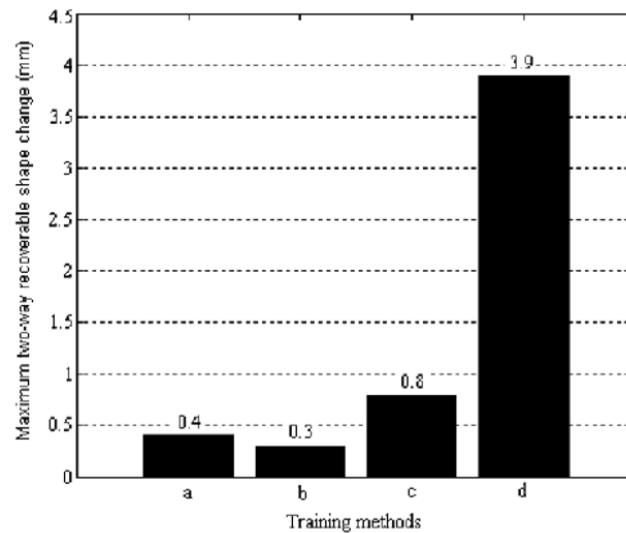


Figure 10. Maximum two-way recoverable shape change obtained by the four training methods.[13]

The plots of the maximum two-way shape change of each specimen. This shows that only method (d) results in a substantial Nitinol TWSMA wire.

2.6 R-phase

The R-phase appears under certain conditions prior to the transformation to B19' phase. The R-phase shows a substantially lower barrier to formation. This transformation is characterized by a sharp increase of electrical resistivity with extremely small temperature hysteresis (1–2 K). In fact the understanding of this phenomenon was controversial for many years including the nature of the phenomenon itself. It was considered to be a precursor or premartensitic phenomena due to displacement waves, which is necessary to create the subsequent B19' martensite structure. However, it is now established from the following reasons that this phenomenon is a martensitic transformation from B2 parent phase to R-phase, which has a distinct crystal structure.

Nevertheless, the effect for B19' phase is larger than that for R-phase, and thus make the transformation temperatures of both phases separable. Several heat treatments were investigated in order to modify the transformation temperatures of alloys object of this study. The objectives went to dislocate the critical temperatures for near room temperature and to avoid the R-phase formation, very common in Ti-Ni alloys submitted to cold work. Despite the several studies of understanding about the R-phase formation in the Ti-Ni alloys, there are yet few applications that could use the narrow ranges of shape recovery presented by this phase. Several research indicate that the presence of the R-phase during martensitic transformation (two-steps, $B2 \rightarrow R \rightarrow B19'$) because matrix phase hardened, hindering the generation of the stress fields associated to dislocation reconfiguration process that facilitate the two-way shape memory effect. The main advantage of suppressing the R-phase formation is to achieve the uniformity in the stress fields, proportioning a better efficiency of the shape memory effect.[8,13]

The study on removing the R-phase is using the calorimetrical of heat treatment. The idea is to treat the samples in difference temperature which are 400°C, 500°C and 600°C with homogenization times of 1, 2, 4, 8, 12 and 24 hours and followed by quench in water at 25°C. For all samples heat treatment at 400°C has showed the normal sequence of phase transformation in the near-equiatomic Ti-Ni wire: ($B2 \rightarrow R \rightarrow B19'$) which can be seen in figure. While for the heat treatment at 600°C gives a clean alone step ($B19' \rightarrow B2$) of Ti-Ni wire.

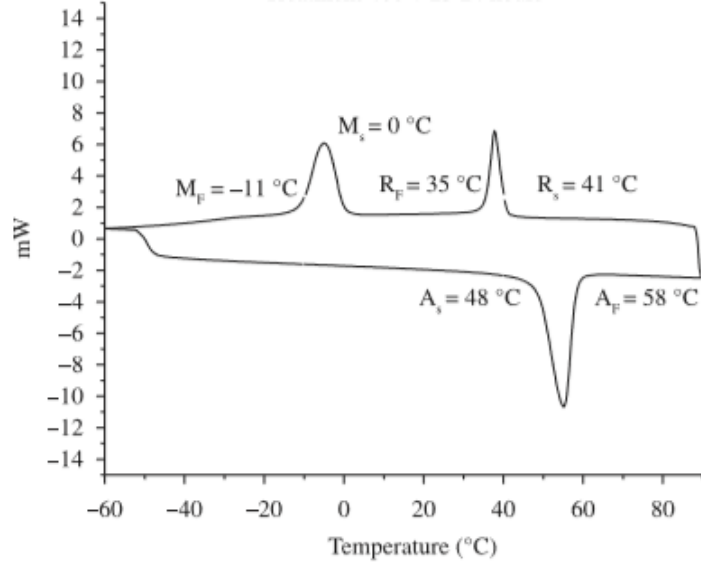


Figure 11. Sample heat treated at 400 °C for 24 hours. [15]

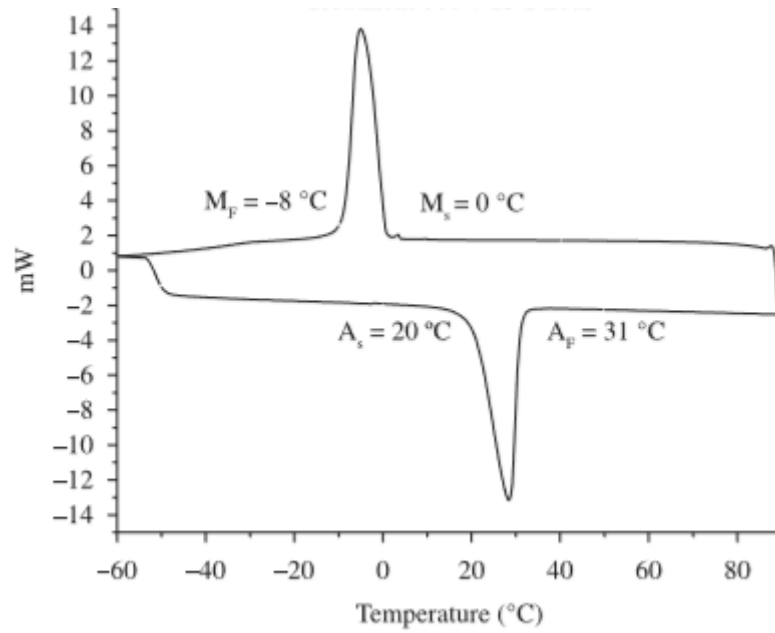


Figure 12. Sample heat treated at 600 °C for 1 hour. [15]

For sample heat treatment at 400°C given in figure 8 has showed the normal sequence of phase transformation in the near-equiatomic Ti-Ni wire: $B2 \rightarrow R \rightarrow B19'$. Observation for the treatment given in figure 9 is stabilization of critical transformation temperatures and enthalpies values independently of ageing time. Back then, the R-phase phenomenon was considered to be a precursor/ pre-martensitic and even a distinct second-order transformation. However, it is now confirmed that the formation of R-phase from B2

is a distinct martensitic transformation; furthermore, the shape memory and superelastic effects are observed in the R-phase, thus confirming the B2→R-phase transformation as thermoelastic in nature. This implies that the B2→R-phase transformation is a competing transformation that appears before the transformation into B19' martensite.

2.7 Precipitation in NiTi alloys

Precipitation in Nitinol can be observe by performing aging heat-treatment studies on Ni-rich Ti-52Ni alloy to investigate the diffusion-controlled transformations using metallographic. The observations suggested that three phases Ti_3Ni_4 , Ti_2Ni_3 and TiNi_3 , precipitate in sequence, depending on the aging temperature and time. In other words, at low temperature and shorter aging time, Ti_3Ni_4 phase precipitates, while at higher aging temperature and longer aging times TiNi_3 phase appears and at intermediary aging temperatures and time, Ti_2Ni_3 phase precipitates. Besides, upon continual aging, the prior-formed Ti_3Ni_4 dissolves into the matrix, and the Ti_2Ni_3 phase increases in both percentage and the precipitates. Continuing the aging further, Ti_2Ni_3 is reabsorbed by the matrix and is replaced by TiNi_3 precipitates.[16]

2.8 Heat treatment

Optimal superelastic properties are typically achieved through a combination of cold work and ageing heat treatments for equiatomic and near equiatomic Nitinol alloys. It should be emphasized that the thermomechanical routes a particular Nitinol alloy is subjected to is dependent on the Ni composition since aging of Ni-rich alloys (Ni > 50.6 at.%) causes precipitation of Ni-rich intermetallic compounds.[16]

Typical thermomechanical history for most medical devices that use shape memory effect Nitinol involves 30-40% cold work followed by heat treatment at 500°C and for shape memory, the preferred heat treatment range is 350°C – 450°C.

2.9 Tensile test analysis

Tensile test is an important feature for understanding the concept of pseudoelastic. Nitinol alloys have a flat unloading curves over large deflections (strains). This allows the design of devices which apply a constant force or load (stress) over a wide range of shapes.

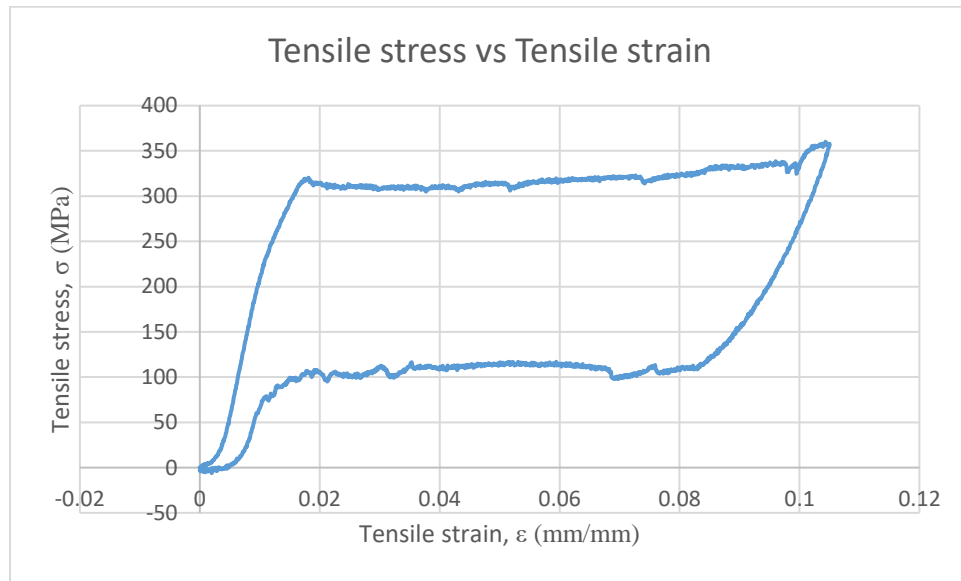


Figure 13. Experimental result of stress against strain.

The graphs in figures 14 shows the pattern of the pseudoelastic and shape memory effect. During loading, phase transitions from austenite into martensite take place. In the case of Nitinol, a nearly horizontal phase transition plateau is often observed if the temperature is approximately constant. After a certain deformation, the phase transition is almost finished and the produced martensite is stretched elastically. During unloading the retransformation occurs at a lower stress level. After loading, the material reaches the initial configuration. Therefore, this material behavior is called pseudoelasticity.

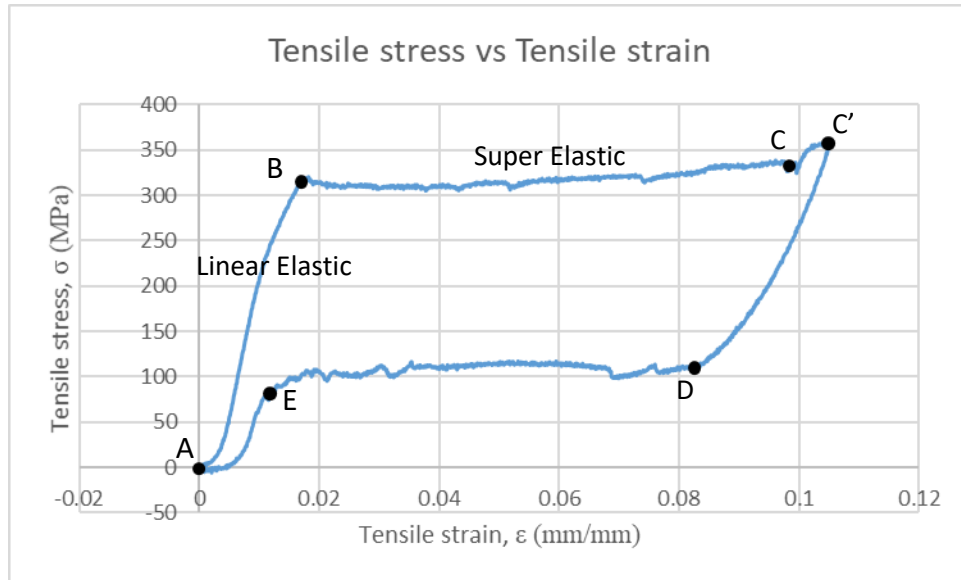


Figure 14: Stress-Strain behaviour for a shape memory alloy (Nitinol).

Table 2. Describing the points of respond in stress-strain graph.

Point	Description
A-B	Elastic deformation
B	Start of reverse transformation of martensite (M_s)
C	Finish of reverse transformation of martensite (M_f)
C'	Unloading
D	Maximum stress for A_s
E	Austenite final (A_f)

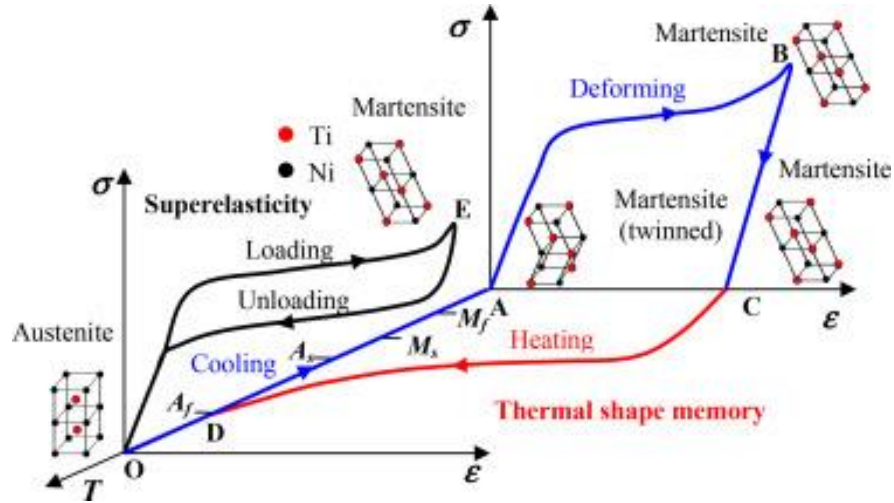


Figure 15. Stress–strain temperature diagram of nitinol.[17]

In the superelasticity region of Fig. 15, Nitinol at first is in an austenitic state at the origin point O. With an applied stress, Nitinol is loaded along path $O \rightarrow E$, where a phase transformation from austenite to martensite and detwinning of martensite simultaneously occur. A large elastic strain up to 8% can be accomplished. Upon unloading along path $E \rightarrow O$, the material transforms back to austenite, and the superelastic deformation is recovered demonstrating a hysteresis loop in the stress–strain diagram.

In the thermal shape memory region of Fig. 15, when Nitinol is cooled down along path $O \rightarrow A$ without applied stress below martensite finish temperature (M_f), complete austenite to martensite (twinned) transformation occurs. The material is plastically deformed through reorientation and detwinning of martensite along path $A \rightarrow B$. Then, unloading from $B \rightarrow C$ causes elastic unloading of the reoriented detwinned martensite and the material stays deformed. After heating above the austenite finish temperature (A_f), the material transforms from martensite to austenite and recovers the pseudoplastic deformation, thus “remembering” its previously defined shape.[17]

Chapter Three: Research Methodology

Firstly, a thoroughly and precise understanding on the connection between behaviour and training of Nitinol shape memory alloy is necessary. Two different pathways, with the intermediate R structure either absent or present, were observed for the transformation from martensitic to austenitic Nitinol, whereas the reverse transformation from austenitic to martensitic Nitinol always included the R structure.

3.1 Differential Scanning Calorimeter Analysis

DSC method yields a plot by measuring the amount of heat given off or absorbed by a sample of the alloy as it is cooled or heated through its phase transformations. In Fig 16. Shows DSC spectra of specimens aged for various times. First of all, the thermograms show austenitic-phase transition during cooling. In particular, on heating, the reverse transformation of the martensite, $M \rightarrow A$, was exhibits, on cooling, at higher heat treatment temperature. The DSC curves show an R-phase transformation during cooling prior to the martensitic transformation, while a reverse martensitic transformation appears during heating. The presence of R-phase is due to cold working and the oxide layer formed during the heat treatment. Therefore, the presence of the R-phase is essential in the characterization of Nitinol alloy wires. From the DSC curves, the transformation start and finish characteristic temperatures were determined by the intersection of a base line and the tangent to a peak.

Table 3. Methods in DSC.

Method 1	Equilibrate at 80.00 °C
Method 2	Ramp 10.00 °C/min to -80.00 °C
Method 3	Mark end of cycle 0
Method 4	Ramp 10.00 °C/min to 120.00 °C