Shape Memory Materials and their applications

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Abstract

A shape memory material (SMM) is a subject that interests both the academic world and the industry [2]. It is a promising subject, a technological challenge and moreover it appeals to the imagination. These materials have the ability to regain their permanent shape after a deformation that seemed irreversible [1]. The shape recovery is triggered by an external stimulus which is mainly a temperature that passes a critical point [3]. But it depends on the specific material which type of energy should be added to trigger the shape recovery. There are for example also materials that are triggered by radiation [2]. The underlying mechanism differs from one material group to another. The shape memory alloys (SMA) use a martensite austenite transformation to achieve the shape memory effect (SME) and the super elastic effect [2]. Shape memory polymers (SMP) on the other hand have different types of mechanisms. The characteristics of the polymer chains or the characteristics of the different phases in the material are responsible for this effect [1]. A SMA gets its permanent shape by heat treatment and the permanent shape of a SMP is in general obtained during fabrication.

This rare phenomenon offers a wide range of possible applications. Imagine for example a damaged car bumper that regains its original shape after a heat treatment. Shape memory materials can also be useful in aerospace applications. The unfolding of antennas or other equipment can be driven by the shape memory effect [6]. The external stimulus can be an electric current that creates Joule-effects in the SMA. This manner of unfolding can result in a weight reduction of spacecrafts or satellites. Another application is a heat engine which uses the SME to convert thermal energy in mechanic energy [4].

Of all the material groups, the shape memory alloys exhibit (in general) better mechanical properties [2]. The best known SMA is a nickel-titanium alloy.

Memory loss is an important concern of the smart technology. A mechanical overload or to many shape recoveries can result in the loss of the permanent shape or an incomplete shape recovery [5].

Key words: Shape memory materials, Shape memory applications, recovery mechanism

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1 Shape Memory Alloys

Shape Memory Alloys (SMAs) are part of the smart materials [14]. The SMAs are able to 'remember' a shape constituted in advance [15]. This shape is the permanent shape. SMAs sense an external stimulus and respond to it by changing their physical properties which results in a deformation or deflection of the structure [11]. The permanent shape returns again. In this way, they are able to undo a deformation that seemed irreversible at first [14]. To achieve this Shape Memory Effect (SME) the SMAs use a martensite austenite transformation. This is further explained with the example of the unfolding of a space antenna. (Figure 1)

A certain heat treatment (example: See 3) is necessary for the space antenna to impose its permanent shape. (d) Afterwards the antenna is deformed in the low temperature phase or the so called martensite phase. (a) The deformed antenna occupies less space which makes it easier to send into space [13]. When launched into space, solar heating will make sure the temperature will be raised above the reverse transformation temperature [12]. This is essential for the antenna to recover its permanent shape [13]. (b-d)

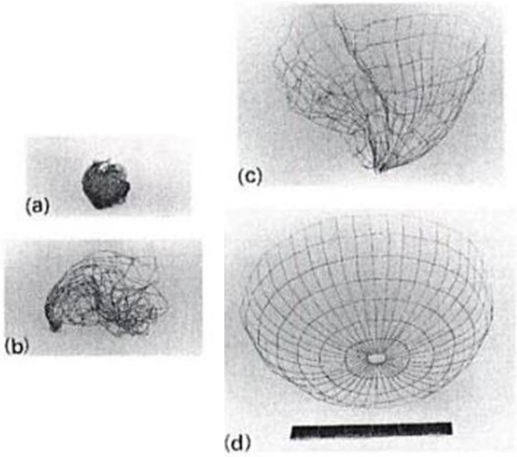

Figure 1 - Demonstration of the SME by a space antenna of Ni-Ti wires. (Courtesy Goodyear Aerospace Corporation) [d]

This way the SMA replaces an actuator and a sensor [14]. This results in a weight reduction which is crucial on an aerospace system [11].

1.1 SMAs and its two phenomena

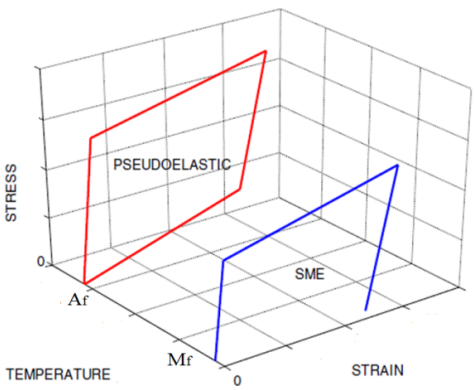

Figure 2 - Stress–temperature–strain diagram to demonstrate SMA behavior in pseudo-elasticity and SME. [c]

1.1.1 Shape Memory Effect

The reversible martensite austenite transformation creates the SME mechanism [15]. This is mainly triggered by passing a critical transformation temperature, but the same result can be obtained by applying stress as an external stimulus [2] [9].

This transition involves a crystal change from a martensite form, which is stable at a low temperature, to an austenite form, which is stable at a high temperature [1] [2] [15]. This transition happens without diffusion, which makes it almost instantaneous [3].

There are four different transformation temperatures that matter when using temperature change as an external stimulus: the martensite start (M_s), martensite finish (M_f), austenite start (A_s) and austenite finish temperature (A_f). These four temperatures are strongly dependent on the applied stress and the material itself [9]. (Figure 4) Each thermal cycle (Figure 3) will lead to micro structural changes and eventually to fatigue behavior and flaw [6].

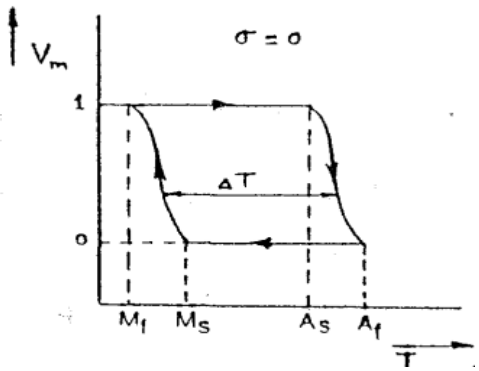

Figure 3 - The martensite austenite transformation.
V_m represents the volume fraction of Martensite. [e]

When stress-free austenite is cooled below M_f (Figure 4: A-B), its structure will switch to 'twinned' martensite whereas the atoms form self-accommodated mirror images or twins of each other [6] [15]. (Figure 5) This is the energetic most favorable state at a low temperature. This causes no associated macroscopic shape change (Figure 8) [6].

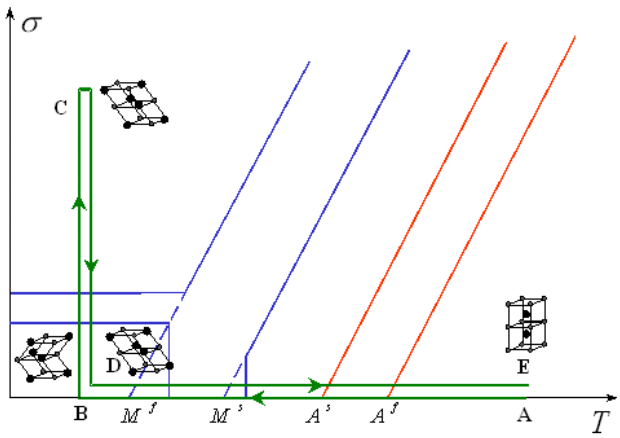

Figure 4 - Schematic representation of the thermo-mechanical loading path demonstrating the SME [a]

When the material is subsequently deformed, the martensite twins are able to reorient the structure in a simple shearing motion as a result of the applied stress [15]. (Temporarily shape C & D) The structure changed from twinned martensite to detwinned martensite. (Figure 4: B-C)

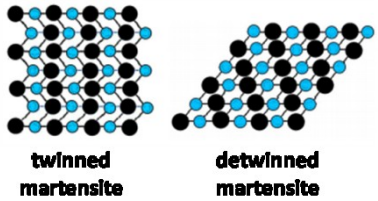

Figure 5 - Detwinning of martensite [f]

Thus the structure is able to compensate this deformation at a stress level far lower than the plastic yield limit of martensite. This is called detwinning and induces a large inelastic strain. This strain induced by detwinning will not be recovered when taking away the mechanical load [3]. (Figure 6) (Figure 4: C-D)

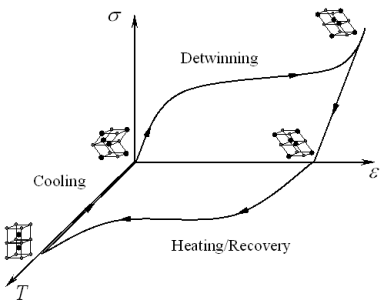

Figure 6 - Stress-strain-temperature diagram exhibiting the SME [a]

Only a large recovery force during the reverse transformation induced by heating (above A_f) can obtain an inelastic strain recovery [9]. (Figure 4: D-E and Figure 6) The recovery force is due to contraction of the structure when transforming from martensite to austenite [6]. This cyclic phenomenon is the shape memory effect. Nitinol for example has a recovery force between 500 and 900MPa [9].

1.1.2 Pseudo-elasticity

When the SMA is at a temperature above the (stress free) austenite finish temperature (A_f), it can transform into the detwinned martensite phase by using stress as an external stimulus [2]. (Figure 4)

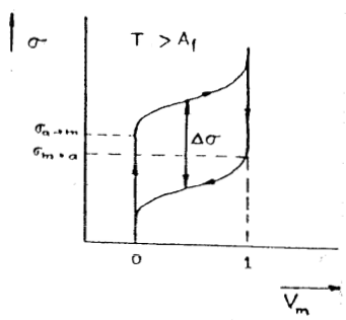

Figure 7 - The martensite austenite transformation by using stress.
V_m represents the volume fraction Martensite. [e]

It is possible to obtain up to 9% strain which can be fully recovered [9]. By unloading, the SMA recovers its original shape by transforming into austenite phase.

This sequence of loading and unloading above A_f is known as pseudo-elasticity or superelasticity [9]. This cycle is not totally elastic because of dissipated energy during these transformations. This dissipated energy is due to internal friction [2].

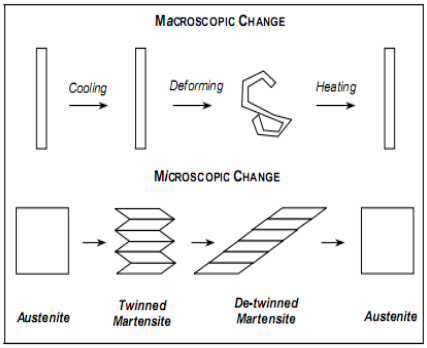

Figure 8 - Overview of the SME [b]

1.2 One way memory effect and two way memory effect

SMAs have two kinds of memory effects. One way memory effect (OWME) and two way memory effect (TWME). OWME is a cycle between a random temporarily shape and a permanent shape. This OWME is only possible in one direction. When the structure is in the martensite phase after deformation by applying a mechanical load (temporarily shape), it can recover its initial permanent shape only by heating above A_f. It is used for a one time actuation application [6]. Such as the earlier mentioned space antenna, this mechanism only has to happen once.

The two way memory effect on the other hand can shift between two permanent shapes. It is possible to impose a permanent shape at a high temperature and another permanent shape at a low temperature. In the future this phenomenon could be used for opening and closing a valve on air- and spacecrafts. To make this thermo-mechanical cycle possible, it is necessary for the material to undergo repeated thermo-mechanical cycles along a specific loading path. This is so called 'training' and can cause changes in microstructure and subsequent changes in material behavior [2] [6]. Locally, intern material will be more and more deformed and adjusted so a certain shape can be imposed and larger strains are achieved. During this training, high temperatures are used so diffusion can occur more easily.

1.3 Memory loss

First of all, it is the permanent shape and not the SME that is lost. Memory loss occurs when a mechanical overload is applied, a strain is passed, too many thermo-mechanical cycles are run trough or when the temperature is too high [14].

An SMA will never return to its exact initial shape. There will always be a certain deviation. If SMAs undergo many transformations, the deviation will increase with every cycle and will eventually lead to memory loss.

Also a deformation above the allowed margin is a cause of memory loss. So recovering its initial shape will be too big of an assignment for the SMA. If larger strains are necessary, it is recommended to 'train' the SMA. (See 1.2)

New originated defects in crystal lattice during thermal and/or mechanical cycling can also hinder the martensite transformation [1].

Memory loss is a main concern of the smart technology and therefore concerns an important matter.

1.4 Applications

Materials and structures in many aerospace systems have mainly been responsible for large performance improvements, because they can reduce the gross weight and operating costs. In the future these systems have to be small, inexpensive and fast. Therefore the self-expanding antenna is only one of many examples that demonstrate SMAs have made inroads in the industrial world.[11]

Another technological challenge is an intelligent, self-healing vehicle where the SMA can be imbedded in the skin or substructures. It can detect damage and respond with an external stimulus for self-repair [11]. A commercial use of this technique can be a damaged car bumper that regains its original shape after heating.

Smart rotorcraft blades and aircraft wings will be one of the first applications of smart material in aerospace [11]. They could increase the maneuverability and controllability by changing the shape of their control surface. In this way it is possible to manipulate lift and twist. Or it can be used to reduce drag [11] [4].

The future will see aerospace vehicles made from programmable multifunctional materials and structures that will have the possibility to adjust their shape and mechanical, electromagnetic, optical and acoustic properties on demand [11] [6].

2 Shape memory polymers

A shape memory polymer (SMP) is able to regain its original shape after a deformation that seemed irreversible. Two sorts of shapes are (in general) distinguishable with the one way shape memory effect. There is a temporarily shape and a permanent shape. The temporarily shape is repeatedly modifiable while the permanent shape is in most cases defined during the fabrication process [7]. The transition between the temporarily shape and the permanent shape is triggered by an external stimulus. The type of added energy that is able to trigger a SMP depends on the specific polymer, but the most common type is thermal energy [10]. Another type of energy that can trigger a SMP is radiation with an electromagnetic wave [8]. (Figure 9)

The SME is not a characteristic of the monomer itself, but results from the structure of the polymer together with the fabrication. This effect is determined by different kinds of polymers with different structures [7]. The structure of a SMP is completely different from the

structure of a SMA. Therefore the underlying mechanism responsible for the SME is also completely different. (Figure 9)

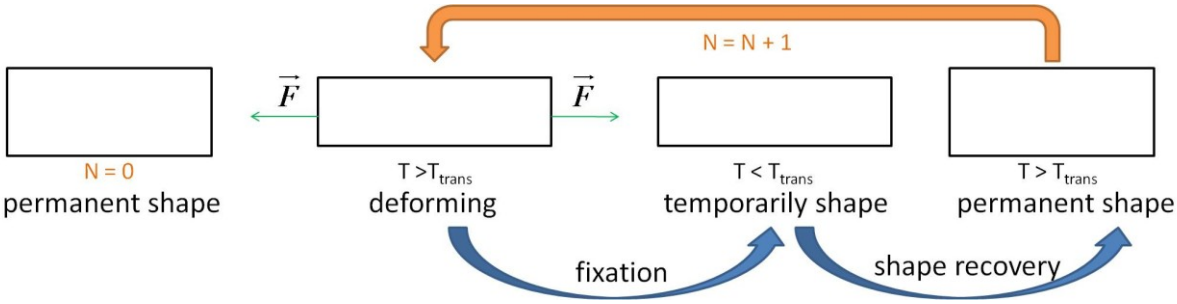

Figure 9 - Principle of the thermally induced one way shape memory effect.

2.1 Thermo-mechanical cycle

The macroscopic behavior can be quantified in several load cases [7]. The following load case is a tensile load. This thermo-mechanical cycle is useful to compare shape recovery and shape fixation properties of different SMPs [8].

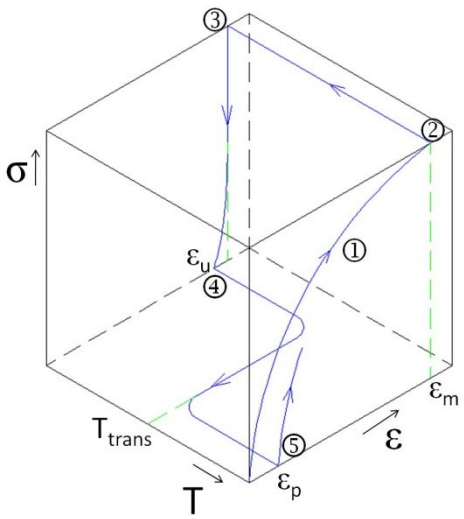

Figure 10 - Graphic results of a thermo-mechanical cycle with a shape memory polymer [7]

- Origin: permanent shape is visible. (σ and ε equals zero)
- ①: Deforming to the desired temporarily shape
- ②: The desired temporarily shape is achieved. $\varepsilon = \varepsilon_m$
- ②-③: Decrease of the temperature below T_{trans}
- ③-④: Removal of the stress by removing the material out of the testing machine
- ⇨ ②-④: Fixation of the temporary shape
- ④-⑤: Increase of the temperature above T_{trans}
- ⇨ Shape recovery [7]

The actual thermo-mechanical cycle shows two imperfections. The difference between ε_m and ε_u indicates that the actual temporarily shape differs from the desired temporary shape. The other imperfection is that after 1 cycle an irreversible plastic deformation ε_p appears. These

imperfections can be quantified in two key figures. These key figures summarize the thermo-mechanical cycle

1) The strain recovery rate is defined as: [7]

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)}$$

The strain recovery rate is a coefficient that expresses how well the permanent shape is approached after the shape recovery process. R_r values above 99% are possible [7]! When this thermo-mechanical cycle is run through N times, $\varepsilon_p(N) - \varepsilon_p(N-1)$ reduces when N enlarge. This is because the polymer chains re-organize in function of the applied deformation during the first cycles [7].

2) The strain fixity rate is defined as: [7]

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m}$$

The strain fixity rate is a coefficient that expresses how less the actual temporarily shape differs from the desired temporarily shape. This coefficient expresses the efficiency of the fixation process.

The work needed to stretch the SMP is stored in the material as latent strain energy during the fixation of the temporarily shape [8]. Therefore the shape recovery process is energetically possible.

2.2 Memory mechanism

There are more groups of thermal triggered SMPs, but only one group is discussed in this paper.

2.2.1 SMP with covalent crosslink's whereby $T_{trans} = T_g$ [7][8]

The flexibility of the polymer chains depends on the temperature. When the temperature is higher than T_{trans}, the polymer chains are flexible [7]. This explains why the polymer is deformed to the desired temporarily shape at a temperature above T_{trans}. When the temperature is below T_{trans}, the polymer chains become rigid and their movements are like they are frozen [7] [8]. The fixation of the temporarily shape is the immobilization of the polymer chains due to vitrification [8]. The transition temperature T_{trans} is in this case the glass transition temperature.

The behavior of the polymer chains is dictated by their urge to seek the most energetically favorable state. Therefore a state with a maximum of entropy is the most probable state because the inner energy is identical for every conformation. The polymer chains are strongly coiled in this state. This most favorable state is achieved when the macroscopic form is the permanent shape which is achieved during fabrication [7]. Note that the temporary shape is less favorable compared to the permanent shape.

The polymer chains don't (or almost not) disentangle or slip during the deformation because of the covalent cross-links between the polymer chains. Therefore the permanent shape is still "remembered" by the material. The permanent shape is fixated by the cross-links who are almost unbreakable. These cross-links are constituted during fabrication (casting, molding …) and therefore the permanent shape is almost not adaptable afterwards [8]. A mechanical overload that breaks the cross-links can be considered as memory loss.

These two properties (cross-links and maximum entropy) explain why the material returns to its permanent shape after a shape recovery. The reason why the polymer chains return to the favorable conditions in terms of entropy is called entropy elasticity [7].

The underlying mechanism of the SME differs slightly from one group of SMPs to another. In general, there is always a reason why the temporarily shape can be fixated and a reason why the shape recovery is possible.
Two examples are:
The reason for fixation can be for example a partial crystallization (instead of vitrification) of the polymer. The transition temperature is in this case the melting temperature [8].
Another example (for SMPs with at least two separated phases) is that the phase with a high melting temperature takes over the function of the cross-links. When the melting temperature of this phase is passed, the permanent shape is resettable, and the "old" permanent shape is lost [7].

3 Experiment: heat treatment at SMA

These experiments consist of a few heat treatments on a cold worked Ni-Ti alloy thread with a diameter of 0.56 mm. The thread did not exhibit a SME before the heat treatment.

3.1 Experiment 1

- The shape of a spring is imposed on the thread. The thread must be hold firmly during the heat treatment because otherwise the imposed shape won't stay in the furnace.
- The performed heat treatment:
    - 8 minutes at 515 °C
    - minimum 90 minutes at 415°C

Observations:

- When the thread was cooled in water after a minimum of 90 minutes at 415°C, the transition temperature of the SMA was above 100°C. (approximately 150°C)
- The transition temperature of a thread that was cooled to ambient air was approximately 50°C.
- The shape memory effect decreased significantly after 5 – 10 shape recoveries.

3.2 Experiment 2

A mold that imposes the thread the shape of a staple was designed. Subsequently the same heat treatment as described in experiment 1 was applied. Because we wanted the transition temperature as close to 35°C as possible, the thread was cooled at ambient air.
The main issue of this experiment is the large deformation during the staple process.

The permanent shape is an open staple, while the temporarily shape is the closed staple. The deformation of the staple takes place in the martensite phase.

Observations:
When the closed staple was heated above approximately 60°C, the closed "legs" of the staple did not completely return (to an angle of 90°). The "legs" of the staple made an angle of 60° instead of 90°. This incomplete shape recovery is due to the very large deformation at the corners of the staple.

To overcome this issue, we applied a technique called "training". We repeated the described heat treatment 4 times. But we didn't observe an improvement.

4 SMP compared with SMA

Both groups of smart materials [14] have different properties. The choice between SMP and SMA (and of course the specific material) depends on the application itself.

The SMPs have much better shape memory properties compared to SMAs.[1] Another advantage of SMPs is their relatively low price. Some SMPs are also biodegradable which can be useful in medical applications. Therefore are SMPs in some cases a good alternative for the more used SMAs [7]. Polymers have (in general) a lower density, lower Young's modulus and a lower melting temperature compared to alloys.

The advantage of the SMAs is their better mechanical properties. Alloys are in general stiffer than polymers. But the SMAs generate also more stress during recovery than SMPs. Guidance values for the generated stress during shape recovery are 1-3 MPa for SMPs and 150-300 MPa for SMAs [8]. This explains why many applications are still made out of SMAs.

5 Literature

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6 Figures

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