

# Shape Memory Alloys

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Shape Memory alloys (SMAs) are materials that have the ability to return to a previous shape or dimension, when subjected to an appropriate thermomechanical procedure. This is made possible by a solid state phase transformation. In the present text we highlight the theory behind the solid state phase transformations that take place in shape memory materials. We then use this to explain the origin of the shape memory effect and superelasticity.

The fabrication of SMAs is essential for the properties of the alloy, therefore we have gone through the general fabrication method for the most used SMAs, the NiTi alloys. The remarkable properties of shape memory alloys have motivated different applications in many fields of science, engineering and even art, and in the last section of this text, we mention a few of the exciting applications.

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## I. INTRODUCTION

Shape memory alloys are fascinating materials with unique properties such as shape memory effect and super elasticity. These properties make them very interesting for applications in many different fields of science and engineering.

A higher quality and reliability in combination with a significant decrease in price has made SMAs more and more common. As a result, SMAs have passed their introductory state and are now enjoying a significant growth. They are an important part of the development of smart materials. A new and highly interesting field.

There are three main kinds of commercial SMAs: CU-based alloys, Fe-based alloys and Ni-Ti alloys. Since Ni-Ti alloys are superior compared to the other SMAs for most commercial applicaitons, we will here, especially in the application part, focus mainly on these alloys.

This text consist of three main parts. The first section includes a thorough description of the martensitic phase transformation, the basis of the shape memory effect and superelasticity. The second section focuses on the different steps of the traditional fabrication method of Ni-Ti SMAs. In the last section we describe representative SMA applications from many different fields, in order to show the diversity and possibilities these materials represent.

## II. THE THEORY BEHIND SHAPE MEMORY ALLOYS.

### A. Martensite and Austenite

The unique properties of SMAs are made possible through a solid state phase change. Instead of solidifying on cooling or liquifying on heating, a solid state phase change means that the molecules in the alloy remain closely packed after the phase transformation and the specimen remains solid. A shape memory alloy therefore has two possible solid state phases; the austenite (or the parent phase) and the martensite phase. Martensite is the phase which exists at lower temperatures. It forms from austenite by displacive transformation when the temperature is lowered below some characteristic temperature  $M_s$ . The atoms in the lattice then move cooperatively from their original phase to the martensitic phase. While the austenite has a cubic structure, the martensite has a lower symmetry structure and is relatively soft and easily deformed(cite int?). The characteristic temperatures for a shape memory alloy phase transition are listed in table I.

TABLE I: Characteristic temperatures of shape memory alloys

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$M_s$	martensite start temperature upon cooling.
$M_f$	martensite finish temperature upon cooling.
$A_s$	reverse transformation start temperature upon heating.
$A_f$	reverse transformation finish temperature upon cooling.
<u>Above this temperature martensite becomes completely unstable.</u>	

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Even though the relative displacements of the atoms are small compared to the inter-atomic distance, a macroscopic shape change occurs. This is shown in Fig. 1 where the two distinct solid phases of a  $CuAlNi$ -alloy are shown. The platelike structure of the martensite is seen in contrast to the smooth structure of the austenite. In the following sections we will describe the martensitic phase transformation in more detail, we will look closer at the crystal structure of austenites, and show why plates may be internally twin related in the martensite phase.<sup>12</sup>.

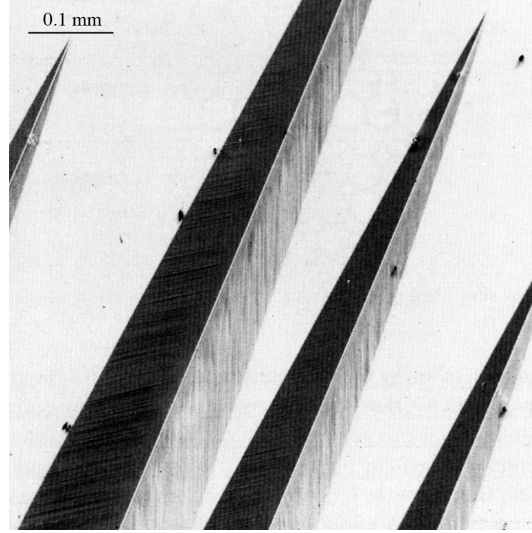


FIG. 1: Optical micrograph of a  $CuAlNi$ -alloy. The smooth, light surface of the austenite is contrasted by the platelike martensite.

### 1. Crystal Structure of the Parent Phase

Most SMAs have superlattice structures where the sublattices of the parent phases are body centered cubic, BCC. They are classified as  $\beta$ -phase alloys and have an electron per atom ratio  $e/a$  close to 1.5. There are also exceptional cases of alloys that have a disordered lattice in the parent phase. Examples of these disordered alloys with face-centered cubic lattices are In-Tl, In-Cd, Mn-Cu and all ferrous alloys (except  $Fe_3Pt$ )<sup>3</sup>.

The  $\beta$ -phase alloys are divided into two types according to the superlattice or composition ratio. The  $\beta_2$  phase, shown in figure 2, has a B2 superlattice (almost BCC, but with different atoms)(Cs-Cl) with about 50 : 50 composition ratio. The  $\beta_1$  phase has a composition ratio of 25 : 75 and a  $Fe_3Al$ -type  $DO_3$  superlattice. The crystal structure of the  $\beta_2$ -phases shown in figure 3. The three dimensional structure is shown in (a), (b) illustrates the atomic arrangement in the (110) plane, while (c) shows the arrangement in the (110) plane above or below the plane in (b). It becomes clear that the cubic structure in (a) can be obtained by alternate stacking of the planes shown in (b) and (c)<sup>3</sup>.

## B. Phase transformation

### 1. The martensitic transformation

The structural change of the austenite occurs by the cooperative movement of atoms relative to their neighbors and is termed displacive transformation. It is dominated by homogeneous lattice-distortive strains, that converts the Bravais lattice of the parent phase into a different one.

The martensitic phase can grow at very low temperatures (Fe-34Ni-0.22C wt% has a  $M_s$  temperature at around 4K), it can also grow at speeds that can be as high as the speed of sound in the same material<sup>2</sup>. Although this does not apply for all SMAs, it makes it clear that the phase transformation cannot be diffusive, as the combination of the often rather low temperature and high speed is inconsistent with diffusion during transformation. The reason to make such a point out of this is to come to some conclusions about the interface plane between the austenite and martensitic phase. As the transformation is diffusionless, it is necessary that the interface has a structure that does not require diffusion, i.e. that it is a glissile interface.

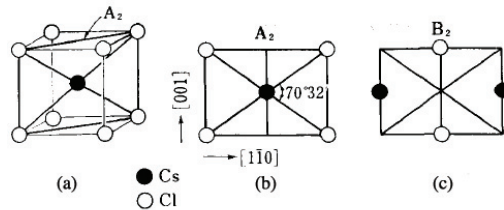


FIG. 2: The crystal structure of the  $B2$  type structure or  $\beta_2$  parent phase. In (a) we see the unit cell, in (b) the (110) plane is depicted, while (c) shows the (110) plane above and below the plane in (b).

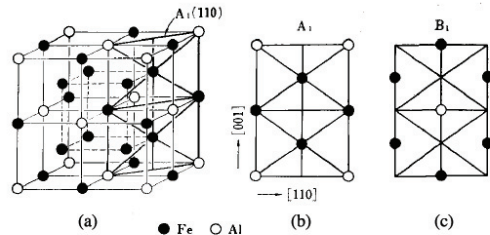


FIG. 3: The crystal structure of  $DO_3$  type structure or  $\beta_1$  parent phase. The unit cell is shown in (a), in (b) we see the (110) plane, while (c) shows the (110) plane above and below the plane in (b). Picture from Miyazaki

Only coherent or semicoherent interfaces comply to this requirement<sup>2</sup>.

If an interface is semicoherent it will contain dislocations that periodically correct the misfit at the interface. If there are more than one array of dislocations, they can interfere and lead to the formation of jogs that render the interface sessile. This leads to a requirement for a semicoherent interface to be diffusionless; it cannot contain more than one array of dislocations. The interface must also include one line that remains undistorted and unrotated by the transformation strain, an invariant line that defines the line vector of the interfacial dislocations<sup>2</sup>.

In 1924 Bain suggested that the change in crystal structure upon martensitic transformation from face-centered cubic parent phase into body-centered cubic martensitic phase could be achieved by a simple homogeneous deformation. The deformation is a result of a strain, the Bain strain matrix  $\mathbf{B}$ , which transforms a vector  $\mathbf{y}$ , into a new vector  $\mathbf{x}$ <sup>12</sup>.

$$\mathbf{x} = \mathbf{B} \cdot \mathbf{y} \quad (1)$$

Although most SMAs in the austenite phase have a BCC structure, the Bain transformation is so simple and general that it will suffice as a description of a martensitic phase transition. It is a displacive transformation where the lattices of the parent and product phases are intimately related. In Fig. 4 one can clearly see both the crystal structure of the parent phase and the crystal structure of the product phase before deformation. The austenite is represented by a face-centered cubic unit cell which can also be represented by a body-centered tetragonal unit cell. The BCT unit cell can be deformed upon a contraction along the  $a_3$  axis and expanded along the  $a_1$  and  $a_2$  axes into a body-centered cubic unit cell of the product phase. We have chosen the  $a_1$ -axis as the  $c$ -axis of the martensite, but we could equally choose the  $a_2$  or  $a_3$  axes as the  $c$  axis. This leads to three possible correspondence variants in the FCC to BCC transformation. The phase transformation shows that the Bain strain consists of a contraction along one axis and identical expansions along the other two axes. It can be seen from the figure that the relationship between the lattice of the austenite and martensite is

$$[001]_{fcc} \parallel [001]_{bcc} \quad [1\bar{1}0]_{fcc} \parallel [100]_{bcc} \quad [110]_{fcc} \parallel [010]_{bcc}. \quad (2)$$

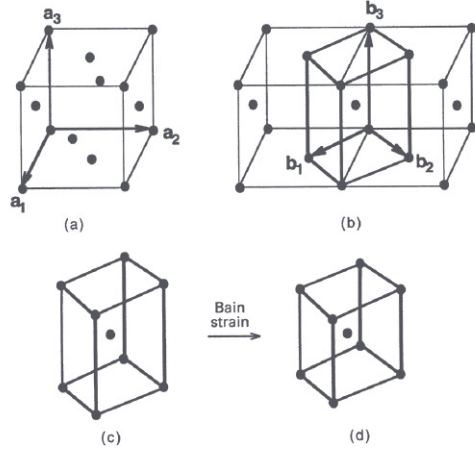


FIG. 4: The austenite lattice shown in (a) is deformed by the Bain strain and is transformed into the BCC martensite lattice shown in (d).

However, this is not observed in experiments. It is still worthwhile examining if the described Bain strain actually leaves at least one line invariant, as this is necessary for the transition to be diffusionless. If the parent phase is represented as a sphere as in Fig. 5, the Bain strain will deform the sphere into an ellipsoid of revolution. It is clear that there are no lines that are left undistorted or unrotated in this figure. However, the lines  $wx$  and  $yz$  are not distorted but only rotated to the new positions  $wx$  and  $yz$ . If the Bain strain,  $\mathbf{B}$ , is combined with a rigid body rotation  $\mathbf{R}$ , the result is an invariant-line strain as  $wz$  and  $yz$  is brought into coincidence. The rotation required to do this also corrects the Bain orientation into what is observed experimentally. But what is also observed is that the habit plane is left both undistorted and unrotated, i.e. we have an invariant-plane strain. Unfortunately, there is no rotation that can turn  $\mathbf{B}$  into an invariant-plane strain - this would require two non parallel invariant lines as illustrated in Fig. 5 (c).

The problem can be expressed in a more compact form; upon transformation a deformation which consists of a lattice invariant strain and a lattice rotation occurs, but the end result is macroscopically represented by an invariant plane strain. However, on applying an invariant-plane strain, the result is a wrong crystal structure. The problem is solved by the phenomenological theory of martensite crystallography(ref, maybe?). If a second shear  $\mathbf{P}_2$  is combined with the first plane-invariant shear,  $\mathbf{P}_1$ , then the correct

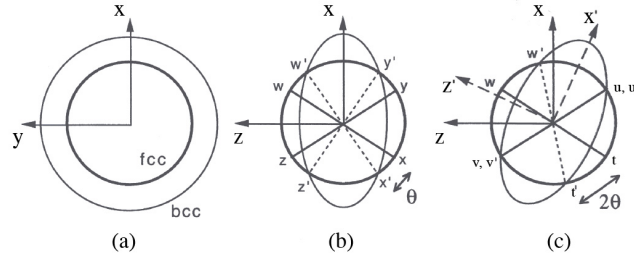


FIG. 5: Illustration of the effect of the Bain strain. When the austenite is undeformed, it is represented as a sphere of diameter  $wx = yz$  in three dimensions (a). The strain transforms the parent phase into an ellipsoid of revolution (b). An invariant-line strain is obtained by combining the Bain strain with a rigid body rotation through an angle  $\theta$  (c).

structure is obtained, but the wrong shape since

$$\mathbf{P}_1\mathbf{P}_2 = \mathbf{RB}. \quad (3)$$

But the discrepancies are all resolved if the shape-changing effect of  $\mathbf{P}_2$  is

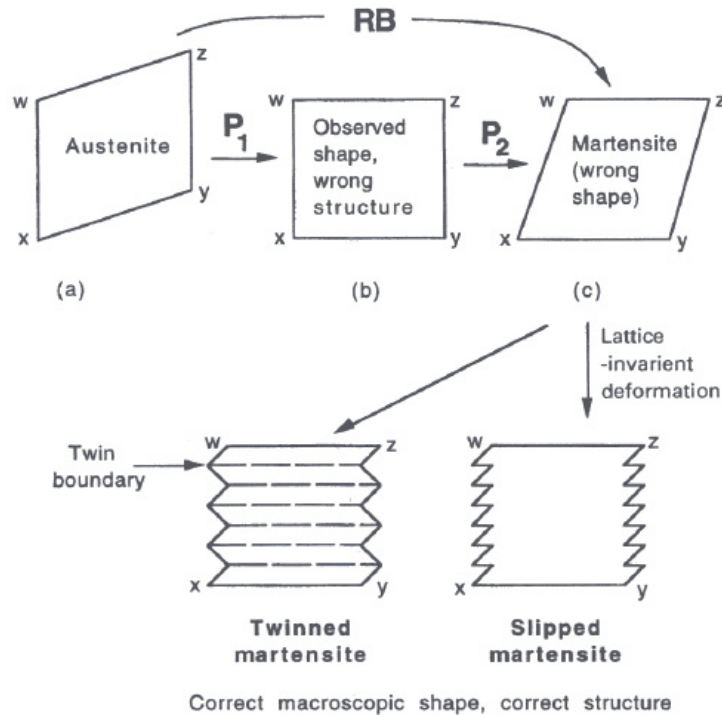


FIG. 6: Illustration of the phenomenological theory of martensite crystallography.

cancelled macroscopically by an inhomogeneous lattice-invariant deformation, which may be slip or twinning, see Fig. 6. And these are observed features of the martensite crystallography. The orientation relationship is

predicted by deducing the rotation needed to change the the Bain strain into an invariant-line strain and we get a substructure in plates of martensite. The strain energy in the martensitic transformation is minimized when the interface between the martensite variant and parent phase becomes an unrotated and undistorted plane. In order to form such a martensite variant it is necessary to introduce a lattice invariant shear such as twins, dislocations or stacking faults. The lattice invariant shear is generally twinning, which is reversible, in the shape memory alloys. Two twin crystals are generally related by a symmetry operation with respect to a mirror plane or a rotation axis.

We will not show the transformations here, but it is worth mentioning that in  $\beta$ -phase alloys the phase transformation takes place as the (110) plane deforms to a nearly hexagonal network and shifts in the  $[\bar{1}10]$  direction by a shear. This results in three different arrangement of atoms in the (110) plane for the  $\beta_2$ -phase, Fig. ?? while the  $\beta_1$ -phase will have six different crystal variants of martensite<sup>3</sup>, Fig. ??.

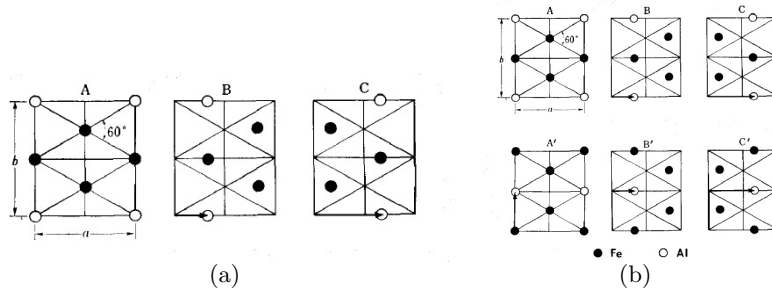


FIG. 7: (a) The three different close packed stacking planes in martensite transformed from a  $\beta_2$  parent phase. (b) By a transformation from a  $\beta_1$  parent phase we get six different close packed stacking planes.

## 2. Thermodynamics of the martensitic transformation

It is worthwhile to examine what drives the martensitic transformation in more detail as martensite deviates from equilibrium in two important ways. It grows without diffusion and inherits the chemical composition of its parent as opposed to an equilibrium transformation where the chemical elements partition into parent and product phases in order to minimize the



free energy. This, however, makes it possible represent the free energy curves of both the parent phase and the martensite in the same diagram as shown in Fig. ???. Here  $G^m$  and  $G^a$  represents the Gibbs free energy of the martensite and the austenite respectively. It is clear that the difference  $\Delta G^{p \rightarrow m}|_{M_s} = G^m - G^p$  will be the driving force for the nucleation of martensite when the temperature is below  $M_s$ . When the temperature is above  $A_s$  we see that the difference in free energy in stead will favor the reversed transformation back to the austenite phase<sup>12</sup>.

The second property that makes martensite deviate from equilibrium is the shape deformation that we have seen is associated with martensitic transformation. This causes strains and it is clear that the resulting strain energy must be accounted for before the transition can happen. If we write the change in the chemical free energy term originating in the structural change from parent to martensite as follows

$$\Delta G = \Delta G_c + \Delta G_e + \Delta G_s = \Delta G_c + \Delta G_{nc}, \quad (4)$$

then  $\Delta G_c$  is a chemical energy term originating in the structural change from parent to martensite,  $\Delta G_e$  is an elastic strain energy term around the martensite, and  $\Delta G_s$  is a surface energy term between parent and martensite.  $\Delta G_{nc} = \Delta G_e + \Delta G_s$  is a non-chemical energy term which in most martensitic transformations is equally large as  $\Delta G_c$ . This is essential as it makes supercooling of  $\Delta T_s$  necessary for the nucleation of martensite and superheating necessary for the reverse transformation.  $M_s$  is not the same as  $M_f$  since the elastic energy around the martensite resists the growth of the martensite unless a further driving force (i.e. cooling) is given<sup>4</sup>.

### 3. Reverse transformation

As described, when a parent phase transforms to a martensite phase, usually many variants of martensites are formed. Similarly, there is no reason why different parent phases may not be formed on reverse transformation. The possible number of variants are restricted to a lower number because martensite has lower symmetry, but why do most martensites revert reversibly to their parent phase? As it turns out, the energetically most

favorable path is the reverse path of the forward transformation. This becomes clear as we examine the crystal structure of the product and parent phase.

If we consider the reverse transformation in an ordered alloy, a typical transformation is ordered BCC to ordered HCP, which is found in many ordered alloys such as Au-Cd, Ag-Cd and Ti-Ni. In Fig. 9 the atom positions in the ordered HCP structure are shown projected on the plane perpendicular to the principal axis. The first layer is represented by large circles, while the smaller circles represent the second layers of the basal plane. Closed and open circles represent the two different types of atoms. The rectangle labeled  $A$  is a unit cell of the ordered structure.

In an ordered structure, the interaction energy between unlike atoms is lower than the interaction energy between like ones. So in the case of an ordered lattice, the three cells  $A$ ,  $B$  and  $C$  will have different energies as only half of the nearest neighbor atoms in cell  $B$  and  $C$  are unlike ones. If now the transformation would occur irreversibly, that is, by transforming the unit cells  $B$  or  $C$ , the original ordered structure would be destroyed Fig. 9 (b). We would end up with a structure with a higher energy than the original parent phase being created. As it is,  $A$  has the lowest energy and will lead to the parent phase with lowest energy upon transformation. This energy

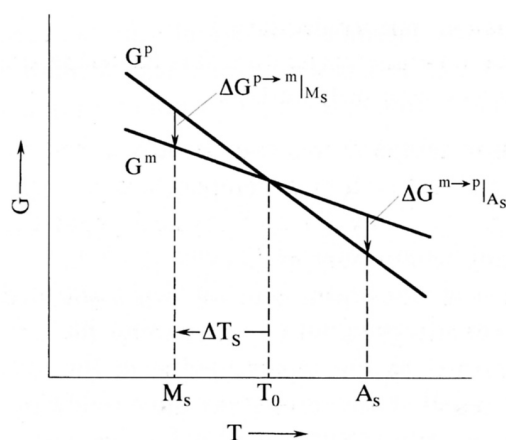


FIG. 8: Gibbs free energy plotted against temperature for the parent phase  $G^p$  and the martensite phase  $G^m$ . The difference in the chemical free energy,  $\Delta G$ , drives the martensitic transformation below  $T_0$  while it drives the reverse transformation above  $T_0$ . From book.

restriction will therefore ensure that a given transformation in an ordered alloy is reversible and guarantees crystallographic reversibility. This is even true under high external stress which opposes the reverse transformations, or in single crystal martensite specimens which devoid stress accumulation to assist the reverse transformations.

However, if the alloy is disordered there is no guarantee for complete reversibility. There is one exception to this statement, and that is the FCC to FCT transformations which is reversible even in disordered alloys. The reason for this is that the lattice correspondence is unique in the reverse transformation because of a very simple lattice change<sup>512</sup>.

### C. Shape memory effect

What characterizes the shape memory effect is that even though a specimen is deformed below  $A_s$ , it can regain its original shape by virtue of heating to a temperature above  $A_f$ . The deformation can be of any kind such as tension, compression or bending etc. as long as the strain is below some critical value, see Fig. 12. The origin of this phenomenon is the presence of the reverse transformation upon heating. As we have seen, martensitic transformations are in general very reversible. A single crystal of the original phase transforms on cooling into several crystals of the new phase. Over-

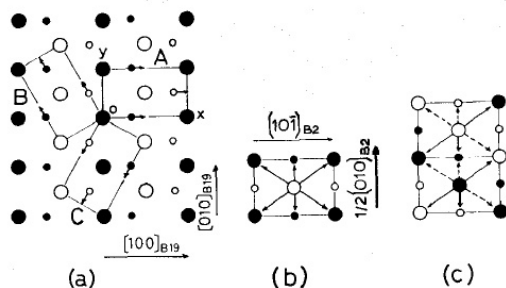


FIG. 9: The reverse transformation from a HCP into a BCC structure is accomplished by a contraction along the  $x$ -direction and an expansion along the  $y$ -direction so that the ratio  $\Delta x/\Delta y$  becomes  $\sqrt{2}$  in cell  $A$ . This is followed by a shuffling indicated by the small arrows. In (a) the three possible lattice correspondences are shown,  $A$ ,  $B$  and  $C$ . The atomic configurations obtained by the reversed transformation for the variants  $A$  in (b) and  $B$  in (c). The projection plane is the  $(101)_{bcc}$  plane. The larger and smaller circles represent atom positions in alternate  $(101)_{bcc}$  planes. The arrows indicated by solid and broken lines represent unlike and like atoms in the nearest neighbor positions, respectively<sup>5</sup>.

simplified, formed martensites are self-accomodated by two or four habit plane variants and each variant contains twins as a lattice invariant shear. The particular crystal variant is favored under the applied stress, the c.v. which gives the largest transformation strain under the stress. The particular variant grows at the expense of others until the specimen becomes the particular single variant if the stress is high enough<sup>12</sup>. The reverse change on heating will then usually result in a single crystal of the same size, shape and orientation as the original crystal. This reverse transformation is driven by the difference in chemical free energy when the temperature is above the reverse transformation start temperature  $A_s$  see Fig. 8. The complete shape recovery is made possible because of crystallographic reversibility, i.e. the original orientation of the parent phase can be restored<sup>3</sup>.

As already stated, the shape memory effect occurs when specimens are deformed below  $M_f$  or at temperatures between  $M_f$  and  $A_s$  above which the martensite becomes unstable. The mechanisms will be slightly different depending on the temperature regime. In the low temperature regime, below  $M_f$ , martensite is formed in a self-accommodation manner as illustrated in Fig. 10. In this process we see clearly that the shape of the specimen does not change as the two crystal variants are twin-related and quite mobile. Under such circumstances, the specimen only remembers the parent phase<sup>12</sup>.

When the temperature is in the intermediate regime, stress induced martensite also contributes to the deformation<sup>12</sup>.

#### **D. Two-way shape memory effect**

We have seen that the martensite remembers its parent phase, and this is sometimes referred to as one-way shape memory effect. In some cases one will observe that it is also possible for an alloy to remember the shape of the martensitic phase. If the applied stress on a sample is too large, an irreversible slip occurs and the shape will not revert to its original shape even when heated above  $A_f$ . However, if the sample is cooled again it will transform into the martensitic phase that is characteristic of the specimen. A repeated heating and cooling will now change the shape of the specimen

between (c) and (d) in Fig. 11. The shape that the specimen remembers now is the martensitic state, and so this effect is called the two-way shape memory effect. The reason that the sample remembers the shape of the martensite is that during such heavy deformations, dislocations will be introduced in the martensite in order to stabilize the configuration of the phase. Upon heating above  $A_f$  and a reverse transformation, the dislocations will still exist in the parent phase, and the stress field around them induces a particular habit plane variant of the martensite upon cooling <sup>12</sup>.

### E. Strain induced martensite or superelasticity

As briefly explained in section IV. A), shear stress always assists martensitic transformations. Thus we can expect stress-induced martensitic transformation above  $M_s$ . Superelasticity is usually realized when a specimen is stressed above  $A_f$ . Stress induced martensite is stable only under stress at this temperature and so it will be unstable in the absence of stress above  $A_f$ . Therefore, no temperature change is needed to transform the alloy. <sup>12</sup>

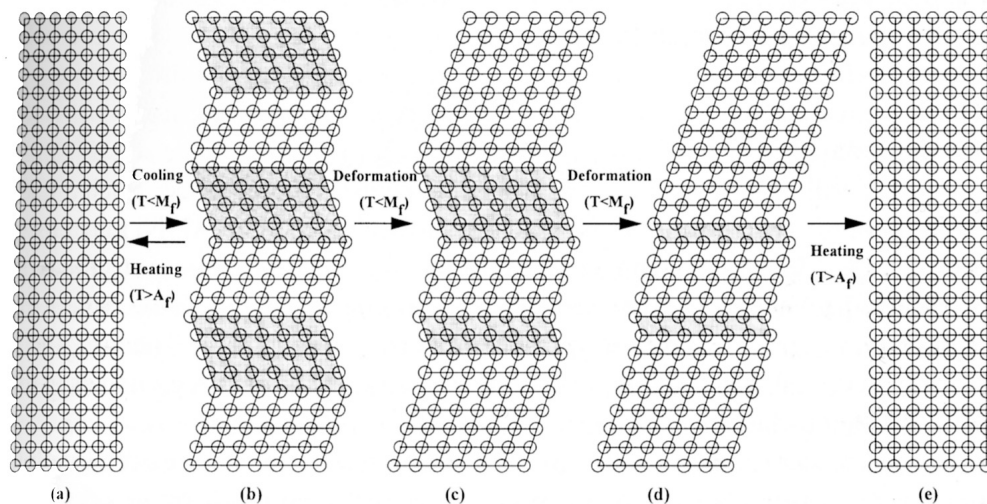


FIG. 10: The shape memory effect illustrated. Starting with the original parent single crystal (a), that is transformed into a self-accommodated martensite (b). The deformation in the martensite proceeds by the growth of one variant at the expense of the other (c-d), i.e. twinning or detwinning. Upon heating above  $A_f$ , each variant reverts to the parent phase in the original orientation by the reverse transformation.

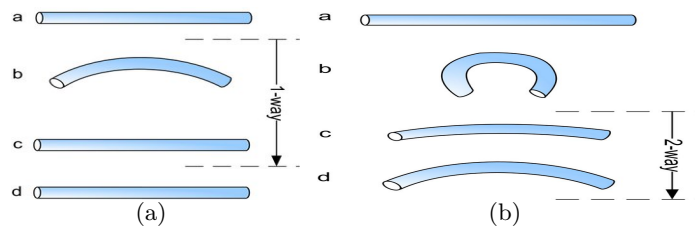


FIG. 11: Illustration of the one-way (a) and two-way shape memory effect (b).<sup>18</sup>

### F. Conditions for good shape memory and superelastic characteristics

We will now consider a few conditions for good shape memory and superelastic characteristics. As seen in Fig. 12, the two phenomena are closely related. In principle they are both observable in the same specimen, depending on the test temperature as long as the critical stress for slip is high enough, as slip never recovers on heating or unloading. Below  $A_s$ , the shape memory effect is observed followed by a heating above  $A_f$ , while superelasticity happens above  $A_f$  where martensites are completely unstable in absence of stress. But in the temperature range between  $A_s$  and  $A_f$  they both occur partially<sup>12</sup>. It is also essential for the conditions for good SME

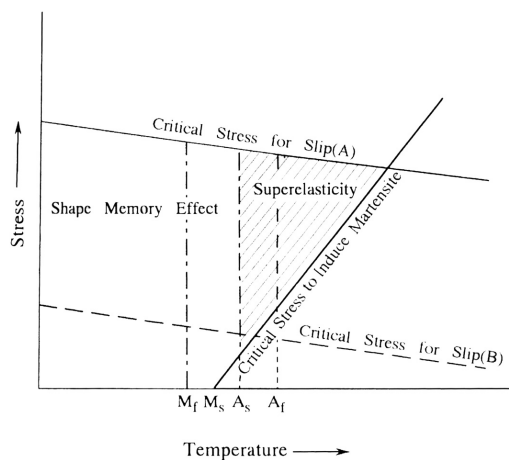


FIG. 12: The regions of shape memory effect and superelasticity in temperature-stress coordinates. Here (A) represents the critical stress for the case of high critical stress while (B) represents critical stress for low critical stress. The reason why the critical stress (A) increases with increasing temperature is that the parent phase is more stable in higher temperature ranges, and thus higher strains are required for stress induced martensite. No superelasticity is realized if the critical stress is as low as the line (B), since slip occurs prior to the onset of stress induced martensite.

and SE effects is that the alloy is thermoelastic. Thermoelastic alloys need only a small driving force for the transformation, this is evidenced by a small temperature hysteresis, which avoids the introduction of dislocations. The origin of the temperature hysteresis is that the transformations on heating and cooling do not overlap. The interface between the martensite and the parent phase is very mobile upon heating and cooling and the transformation is crystallographically reversible as the martensite reverts to the parent austenite in the original orientation. This transition is called thermoelastic. When the driving force is very large it implies that the interface between martensite/austenite is immobile once the martensite has reached a critical size. The reverse transformation occurs by the nucleation of the parent phase and is therefore not reversible<sup>12</sup>.

We can simply sum up the essential conditions for the realization of shape memory effect and superelasticity as crystallographic reversibility of martensitic transformations and the avoidance of slip during deformation in a thermoelastic alloy. From this it becomes clear that by hardening the alloys and increasing the critical stress for slip the characteristics of the shape memory effect and superelasticity are improved<sup>12</sup>. However, there are still some difficulties with shape memory alloys as many of them have poor fatigue properties; this means that while under the same loading conditions (i.e. twisting, bending, compressing) a steel component may survive for more than one hundred times more cycles than an SMA element<sup>4</sup>.

### III. FABRICATION

Fabrication of shape memory alloys consist of several steps. Fig. 13 shows the steps of the traditional fabrication of Ni-Ti SMAs, which is similar to the traditional fabrication of other SMAs. In the following of this chapter we will have a closer look at each of these steps, and the end of the chapter will have a brief look at a newer fabrication method, the method of powder metallurgy. Initially there were a competition between Cu based and Ni-Ti based SMAs. This resulted in detailed research, which in the end showed that Ni-Ti based alloys are superior over Cu based alloys for most applications.<sup>11</sup> For that

reason we will here, in this section and the next section, focus mainly on applications of Ni-Ti SMAs.

### A. Melting and casting

There are several possible melting methods for Ni-Ti alloys, including high frequency induction melting, electron beam melting, argon arc melting and plasma arc melting. The preferred melting method in most cases is induction melting. The induction of alternating currents has a mixing effect that makes the alloy more homogeneous.<sup>12</sup> Another advantage of the induction melting is that the chemical composition is well controlled. As a result the transition temperature, which is strongly dependent on alloy composition (one percent shift in nickel content results in a 100K change in the transition temperature of the SMA.), can be controlled within  $\pm 5$  K.

Since molten titanium is very easily oxidized, Ni-Ti alloys have to be melted in high vacuum or an inert gas atmosphere.<sup>12</sup>

### B. Hot- and cold-working

After the Ni-Ti ingot is made by melting and casting, it has to be forged and rolled into a bar of a suitable size.

Hot-work like forging and rolling is optimal at a temperature around  $1073^{\circ}\text{C}$ .<sup>12</sup> The workability of the alloy is improved at higher temperatures, but the material is also easier oxidized.

The next step for the alloy is cold-working, most commonly wire drawing. Cold-working of Ni-Ti alloys is much more difficult than hot-working. One reason for this is that work hardening occurs readily. As a result constant annealing is usually required. For the wire drawing to carry out satisfactory, it is important to have an optimal combination of the drawing and the annealing process.<sup>1</sup>



FIG. 13: The different steps in fabrication of NiTi-SMAs.



Machining, and especially drilling, of Ni-Ti alloys is very hard. Conventional methods are possible to use, but high wear on tools is very common. It is possible to weld Ni-Ti alloys, but the joints tend to be very brittle.

### C. Forming, shape memory treatment and finishing

In the end the cold-drawn wire is formed to its final shape, e.g a cylindrical spring. This can for instance be done by a coil forming machine.

The last process of Ni-Ti fabrication is shape memory treatment. The most common treatment is the "medium temperature treatment". In this procedure the formed spring is first attached to a jig and then heated to memorize the shape. The heating temperature and time of heating is adjusted to fit the requirements of the product. It is important to control the treatment temperature since the shape memory characteristics is strongly affected by this temperature.<sup>12</sup>

Different Ni-Ti products require different a finishing. When needed metal plating are used to make the surface of the SMA appear more beautiful and surface coatings are used for some wires e.g bra supporting wires. However, no treatment for corrosion protection is needed, because the Ni-Ti alloy possesses excellent corrosion resistance, due to a protective titanium-oxide (TiO<sub>2</sub>) layer.

### D. Powder metallurgy

Powder metallurgy is a newer and more sophisticated fabrication method than the one describes previously.

There are two kinds of power metallurgy techniques for Ni-Ti alloys: raw metal powder sintering and alloy powder sintering. The first method uses pure metal powders, while the second method uses a pre-alloyed powder. The homogeneity of the sintered alloy is better with the second method.<sup>12</sup>

In the fabrication process the powder is injected into a mold. Then pressure and high temperatures are applied for a long time until the product is finished.

Powder metallurgy does not involve a melting process that causes inac-

curacy in the alloy composition. Hence, the transformation temperature of the alloy can be well controlled.

#### IV. APPLICATIONS

The unique properties of SMAs have been known since the beginning of the 1930's. Nevertheless, it was first after the shape memory effect was discovered in a Ni-Ti alloy in 1962 that SMAs attracted some commercial and technological interest<sup>7</sup>. Ni-Ti SMAs showed a larger recoverable strain energy and a larger active temperature range than other SMAs known at that time.

Although other reversible phase change materials were known at the time, the Ni-Ti alloys showed a large recoverable strain value when compared to other binary, ternary or quaternary shape memory alloy systems.

The original nickel-titanium alloy has some of the most useful characteristics in terms of its active temperature range, cyclic performance, recoverable strain energy and relatively simple thermal processing. Ni-Ti and other alloys have two generic properties thermally induced shape recovery and super- or pseudo-elasticity. The latter means that an SMA in its elastic form can undergo a deformation approximately ten times greater than that of a spring-steel equivalent, and full elastic recovery to the original geometry may be expected. This may be possible through several million cycles. The energy density of the alloy can be used to good effect to make high-force actuators - a modern DC brushless electric motor has a mass of 5-10 times that of a thermally activated Ni-Ti alloy, to do the same work.

The first large scale industrial application of SMAs was a Ni-Ti coupling developed during the 1960's for the Grumman F-14 airplane.<sup>12</sup> The Ni-Ti couplings were chosen because of their light weight and reliability, despite the fact that they were expensive. Since SMAs were very expensive at this time, it was difficult to find a market for commercial use of SMAs. However, some small niche markets, like the US defense world, existed. Here higher prices were accepted when the performances were superior.

In 1975 the first SMA medical device was made, an orthodontic implant.<sup>6</sup>

This was the start of a new epoch for commercial applications of SMAs. The unique properties of SMAs were ideal for developing new medical devices and refining existing treatments. Today medical applications probably accounts for the largest dollar value of SMAs.

In the 1980's Japanese companies were successful in SMA technology, and the result were commercial applications in products such as air conditioning vents and bra wires.<sup>17</sup>

Because of the great properties of SMAs, many people are eager to use them. However, since SMAs are still relative expensive and difficult to fabricate, it does not always represent the best commercial solution. It should for each new product be considered if SMAs produces an unique solution for the spesific use. If not, it will normally be cheaper and easier to use a solution based on a normal material and another mechanical design.

Today SMAs are being applied in a wide range of different fields from microactuators in space and cardiovascular devices to eye glass frames and jewelry. In the following sections we will have a closer look at some of these applications, starting with the important field of medical applications.

### **A. Medical applications**

Medical applications of shape memory alloys have been a great technological and commercial success. From the first SMA orthodontic implant was made in 1975 until today the use of SMA for medical applications has been rapidly growing.<sup>6</sup>

Materials used for medical applications needs to satisfy two important demands: biofunctionalbility and biocompatibility. The biofunctionability of a material refers to the ability of the material to perform the desired function in the body for the expected period of time.<sup>12</sup> Biocompatibility refers to the ability of the material to be nontoxic during it's period implanted in the body.<sup>6</sup>

Among all shape memory alloys, Ti-Ni based alloys are mainly used for medical applications.<sup>9</sup> Ti-Ni alloys are considered to be the best because of their superiority in mechanical stability, biofunctionability and biocompati-

bility.

Since nickel is a highly poisonous element, several studies has been carried out to investigate the biocompatibility of Ni-Ti alloys.<sup>6</sup> Resulting literature reviews generally indicate that Ni-Ti alloys has extremely good biocompatibility. This is due to the formation of a passive titanium-oxide ( $\text{TiO}_2$ ) layer, similar to that found on Ti alloys, which produces a physical and chemical barrier against the oxidation of nickel.<sup>7</sup>

In the rest of this section some concrete medical applications of SMAs will be presented.

### *1. Cardiovascular devices and surgical instruments*

Cardiovascular devices and surgical instruments based on shape memory alloys play an important part in the general trend of less invasive surgeries in medical therapy<sup>7</sup>. Less invasive surgeries are important in order to minimize patient risk.

The first cardiovascular device developed using a SMA was the Simon vena cava filter showed in Fig. 15<sup>6</sup>. By filtering the blood in the vena cava vein, a large vein that carries de-oxygenated blood from the upper half of the body to the heart's right atrium, the Simon filter prevents blood clots from reaching the heart and cause serious hazard. The legs and the "flower" of the filter trap the clots arriving with the bloodstream, which are then dissolved over time.<sup>7</sup> The major users of this filter are persons who cannot take anticoagulent medicines.

The insertion of the filter into the human body exploits the shape memory effect. The filter is cooled down and deformed in its martensitic state, and then attached to the tip of a catheter. Afterwards the filter is placed inside the body while a saline solution is flowing through the catheter to keep the temperature low. When the filter is released from the catheter the flow of the saline solution is stopped. Hence the bloodstream will heat the filter, and the filter will return to its original shape. This procedure is shown in Fig. 15.<sup>6</sup> Another important and successful cardiovascular application is the self-expanding stent, which is used to maintain the inner diameter of

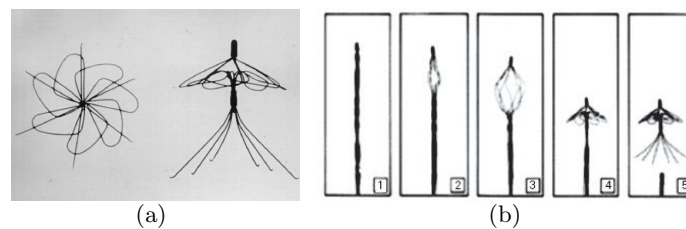


FIG. 14: (a)The Simon filter as it looks when it is expanded in the vein.(from duerig)  
 (b)The procedure of releasing the Simon vena cava filter. Picture 1 shows the filter in it's deformed state inside the catheter. The following pictures shows how the filter expands as it is released from the catheter. In the last picture the filter has returned to its original shape.<sup>6</sup>

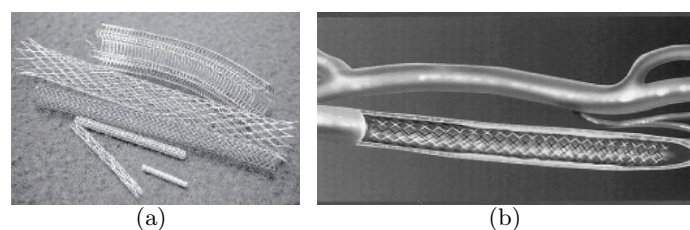


FIG. 15: (a)Different Ni-Ti self-expanding stents.(from machado)(b)A self expanding stent inside a blood vessel, keeping the vessel open and maintaining the blood flow.<sup>7</sup>

a blood vessel.<sup>9</sup> As with the Simon filter, the stent is cooled down and compressed in its martensitic state and then delivered to the target place in the body using a catheter. When the stent is released from the catheter it expands as a result of heating from the body. The stent exert a constant pressure on the blood vessel walls to avoid any obstacles in the bloodstream. Fig. ?? shows an example of an self-expanding stent.

## 2. Orthopedic implants

Ortopedics is an attractive field for application of Ti-Ni shape memory alloys. Applications include the spinal vertebra spacer, orthopedic staples and bone plates<sup>6</sup>.

Bone plates are used to support and speed up the healing process of broken and fractured bones. Usually they are applied to areas where casts cannot be applied, like facial areas. The bone plates are attached to the broken bones with screws as shown in Fig. 16. By exerting a constant

pressure on the fracture the bone plates help to compress and fix the broken bones. Normally bone plates are made of titanium or stainless steel. These



FIG. 16: (a) A SMA bone plate fixed to a human jaw. (b) Detailed picture of a SMA bone plate and a screw.<sup>8</sup>

bone plates will only exert a pressure on the fracture for a couple of days, afterwards the tension is lost due to low flexibility of the material. The advantage of bones plates made of superelastic SMAs is that they can apply a constant pressure on the fracture for a longer amount of time and hence speed up the healing process significantly.<sup>8</sup>

The SMA bone plates are first deformed, and then attached to the fracture. Because of the shape memory effect they tend to recover their former shape when they are heated. By choosing an Ni-Ti alloy that has a transition temperature below the body temperature the plates will constantly try to transform back to their original shape and thereby exert a constant pressure on the fracture.<sup>6</sup> The constant pressure can be regulated by adjusting the alloy composition and the manufacturing process.

### 3. Dental applications

One of the most successful dental application of shape memory alloy is the dental arch wire which utilizes the long-time constant force generated by the superelastic effect.<sup>12</sup> Other interesting applications include dental implants and attachments for dentures which use the shape memory effect. Here we will only take a closer look at SMA dental arch wires.

Traditionally many different metal and alloys have been used for dental arch wires. For the teeth to move optimal, it is important that the force from the wire is in the optimal force zone. In the excessive force zone, above the

optimal force zone, tissue damage may occur. And in the suboptimal force zone the teeth do not move efficiently. Fig. 17(a) shows a stress-strain curve for an elastic dental arch wire with a high elastic modulus (like stainless steel), where the effective strain range corresponding to the optimal force zone is small. When an alloy with a low elastic modulus is used, the effective

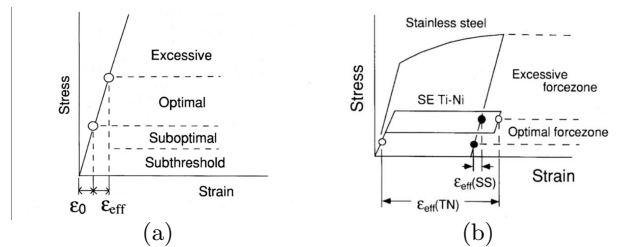


FIG. 17: Schematic stress-strain curves: (a) for an elastic dental arch wire with a high elastic modulus, where the effective strain range corresponding to the optimal force zone is small. (b) for stainless steel and Ni-Ti wires, where the optimal force zone for the Ni-TI wire is much larger than for the stainless steel wire.<sup>12</sup>

strain range increases, which means the the optimal force zone increases. This is shown in Fig. 17(b) where the stress-strain curve for stainless steel and superelastic Ni-Ti are compared. Superelastic Ni-Ti wires are such low elastic modulus materials and are hence very suitable for dental arch wires.

Compared to stainless steel arch wires the Ni-Ti arch wires are applying a more gentle and constant pressure over a longer period and are thus much more comfortable to wear, and physiologically more favourable for teeth movement<sup>13</sup>. In addition Ni-Ti arch wires do not have to be re-tensioned as often as stainless steel wires resulting in less visits to the orthodontist<sup>14</sup>.

## B. Non-medical applications

Today medical technology is the largest market for applications of SMAs. Nevertheless, there also exist many different niches for interesting and successful non-medical applications of SMAs. These include everything from technical applications like couplings, fasteners and actuators, to shoe implants and art sculptures.

In this section we will have a closer look at some of these applications.

### 1. *Shape memory alloy actuators*

The most important non-medical application of SMAs is actuators. A shape memory alloy actuator is one type of thermal actuator, which is a device that can convert thermal energy into mechanical energy. It exploits the shape memory effect to generate a force that can be used to perform work.<sup>12</sup>

When compared to other types of actuators like metal thermostatic elements and wax actuators, shape memory alloy actuators show many advantages<sup>11</sup>:

- *Simplicity of mechanism*

Only the phase transformation of the alloy is used for the actuator mechanism. Hence many designs are possible. Shape memory actuators can work in many different deformation modes, such as tension, rotation and compression.

- *Clean and quiet operation*

Friction mechanisms can be avoided, hence production of dust particles can be avoided. Since there is no vibrating parts all movements occur extremely silently.

- *High power/weight and power/volume ratios*

This makes shape memory alloy actuators very attractive in micro-actuator technology.

But some drawbacks also have to be considered:

- *Low energy efficiency*

The energy efficiency of turning heat into mechanical work is very low.

- *Degradations and fatigue*

The characteristics of a SMA changes over time when used. The shape can only be recovered a certain amount of times.



As a result, SMA actuators are still a niche product and are not produced in large scales, despite some of the great advantages.

Shape memory alloy actuators have a wide range of application possibilities, which can be divided into two groups:

- Actuators that act as both sensor and actuator. The phase change in the shape memory alloy is triggered by the temperature of the environment.
- Actuators that are heated by an external source and then perform the required action.

Applications of the first kind can be found in safety control devices: water kettles, coffee makers, thermostatic mixing valves, air flow control for an air conditioner and etc.

The working principles of these devices are similar. As an example, a sketch of a thermostatic mixing valve is shown in Fig. 18. As for most shape memory alloy actuators the shape memory alloy element is a coil spring. This coil spring is opposed by a bias spring. In Fig. 18 the shape memory alloy spring is exposed to the flow of the mixed water. When the temperature of the mixed water is too high, the SMA spring expands and pushes the spool to the left. This allows for more cold water and less hot water to flow, hence the temperature of the mixed water is reduced. The reverse mechanism occurs when the water is too cold. The control knob determines the delivery temperature by changing the compression on the bias spring.<sup>12</sup> SMA actuators which are heated by an external source, hence belonging to the second group, are very interesting for robotic applications.<sup>11</sup> One example is underwater exploration robots. The Ni-Ti SMA has excellent sea water corrosion resistance and the electrical resistance of Ni-Ti is much lower than sea water<sup>12</sup>. As a result it is possible to electrically energize the actuators without having current leakage to the surroundings. Therefore the actuator wires can be bare and the difficult task of sealing conventionally actuators is avoided.

The simplicity and high power to weight ratio of SMA actuators makes them, as mentioned previously, very attractive in micro-actuator technology,

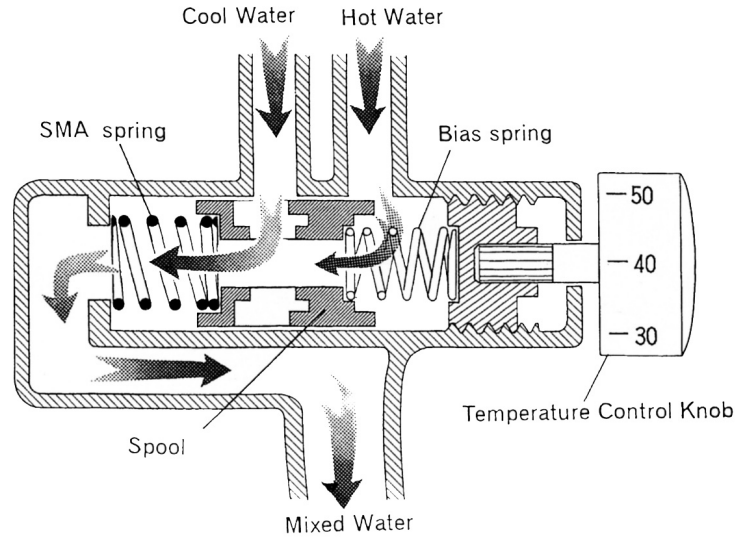


FIG. 18: Sketch of a thermal mixing valve with a shape memory spring.<sup>12</sup>

which is a rapidly growing field. One example is a micro robot that contains SMA actuators that is heated by a photon beam. The use of SMAs eliminate the need for batteries, allowing miniaturisation. And the heating by a photon beam also eliminate the need for wires and batteries. This technology has made it possible to make micro robots which are 2 microns wide and 10 microns long, 50 times smaller than what is possible using conventional actuators.<sup>16</sup>

The high power to weight ratio also makes SMA very interesting for space applications. Clean operation also is very important in space, something which is provided by SMA actuators.

## 2. Fashion and gadgets

For fashion and gadgets SMA has been applied successfully for many years. Eye glass frames made of SMAs are very popular. The combination of stiffness and super-elasticity makes the glasses comfortable to wear and more robust. The same combination of stiffness and super-elasticity were also exploited by Sony in the headband of their "Eggo" headphones. Because of the superelastic effect the headphones are very comfortable to wear and can be folded up into an egg shape (hence the name).<sup>12</sup>

Superelastic wires have also been used as the core wire of a wedding



FIG. 19: The sculpture *Hermaphrodite* by Jean-Marc Philippe. It is made of a Cu-Zn-Al alloy and it is reversible transformed from a man's torso at 20°C into a woman's torso at 55°C.<sup>15</sup>

dress petticoat, allowing the the petticoat to be folded into a compact size for transport. And they have been used in shoes to make them fit perfectly and prevent them from being worn out.<sup>17</sup>

### 3. Other interesting applications

One recently introduced application for SMA is in the protection of historical monuments from damage caused by earth quakes. A special wire consisting of many thin Ni-Ti wires with different nickel and titanium composition (hence different transition temperature) has been developed. Together the thin wires form a thicker wire that is capable of supporting the historical monuments over a large range of temperatures. The metal wires can either be wrapped around the monuments from the outside or support the monuments from the inside. Some of the energy from an earth quake will be turned into heat that will trigger the shape memory effect in the supporting wires.<sup>10</sup>

Finally, it is worth to mention that even artists see fascinating opportunities using SMA. Fig. 19 shows the art-work *Hermaphrodite* by the French artist Jean-Marc Philippe. The sculpture exploit the temperature dependence of the shape memory effect. In the shade the sculpture represents a

man's torso, but in the sun it is transformed into a woman's torso.<sup>15</sup>

## V. CONCLUDING REMARKS

In this text we have tried to give a short and basic introduction to the field of shape memory alloys. The purpose of this text is not to give a complete analysis of all aspects concerning SMAa, but rather to describe in general some features that we find to be important.

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