

SHAPE MEMORY METAL ALLOYS IN THE CONTEXT OF TEACHING SMART MATERIALS

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ABSTRACT

Compared to other equally consequential material types, smart materials are fairly glossed over in general Materials Science and Engineering instruction. Shape memory metal alloys (SMAs), a subset of smart materials, are therefore among the subjects deserving more attention. Pragmatically, they ought also to have more emphasis as they are a topic likely to intrigue and hold the interest of students owing to their somewhat amazing behavior. Such alloys exhibit two closely related but distinct phenomena: shape memory and superelasticity (also called pseudoelasticity). Shape memory is the capability to undergo deformation at one temperature followed by recovery of the original undeformed shape upon heating above the characteristic transformation temperature. The phenomenon of superelasticity, in which a material sustains much higher than typical strain with a fully elastic recovery, occurs within a narrow temperature range just above the transformation temperature. Because SMAs are widely used in applications ranging from dental wires and arterial stents to fire security systems and helicopter blades, there have been many experimental and theoretical studies performed to explore their strength and fatigue behavior, especially of nickel titanium (NiTi) shape memory alloys, which are common among SMAs. A familiar example is the NiTi alloy known as nitinol. This and other such alloys, having now an established presence among engineering materials, merit corresponding attention in education, particularly on aspects of fatigue, mechanical performance, and biomedical application. Over time, a variety of defects can form in SMAs, and accumulation of those defects ultimately causes internal crack formation and propagation. In this article we present a review and summary of the mechanisms of behavior of shape memory alloys, limitations—and underlying reasons for them—of SMAs, applications—potential and realized—of SMAs, and we draw connections among these features in order provide a more encompassing description of such alloys for better educational instruction.

Keywords: *Nitinol (NiTi), shape memory alloys, defects, nickel (Ni), titanium (Ti), interstitial interaction.*

1. INTRODUCTION

The first report of shape memory alloys (SMAs) appears to be by Kurdyumov and Kaminsky in 1936¹, as reviewed, for instance, by Hornbogen². Attempts to assign the discovery to later work such as that in 1938 by Greninger and Mooradian³ have also been made. The shape memory effect consists of returning to the original size and shape after large deformations. This is contrasted with reversible deformations for magnetostrictive materials, which entail strains (ϵ) no larger than 1%, and for electrostrictive materials with ϵ less than 0.1%.

Apart from SMAs, shape memory polymers (SMPs)⁴ exist also, but are outside the scope of the present article. Shape memory ceramics do not exist because the elastic region in which strain is linearly proportional to stress practically ends at the point of fracture. Both SMAs and SMPs belong to a broader category of *smart materials*. Smart materials are defined as those that respond in a significant and predictable manner to external stimuli such as temperature change, pressure change, magnetic field imposition (or change), electric field imposition (or change), and so on⁵. In this article we shall discuss the mechanism of behavior of SMAs, limitations in the use of these materials and the reasons for these limitations, and also current and potential applications. A widely used SMA is nitinol, which contains approximately equal atomic percentages of nickel and titanium and which will be used in various locations below as an example. Although nitinol is the most common SMA, other Ni-rich and Ti-rich alloys are also used as well as Cu-Zn and ternary alloys such as Ni-Cu-Ti or Ni-Hf-Ti.

Nickel titanium (NiTi)-based alloys have been used in multi-field applications due to their excellent structural and functional properties, the latter including shape memory and superelasticity. As already indicated, shape memory is the ability of a material, once deformed, to remember its original shape and return to it if heated to its transformation temperature. The phenomenon of super-

elasticity, perhaps somewhat less familiar than that of shape memory, involves strain accommodation, occurs without any change in temperature, and takes place at temperatures (slightly) above the shape memory transformation temperature. In shape memory metal alloys (SMAs), both effects involve phase transformation between austenite and martensite phases of the alloy; see Figure 1. As noted by Katherine Chen and her colleagues^{6,7}, cooling—resulting in full transformation of austenite to martensite—leaves the bulk macroscopic shape intact.

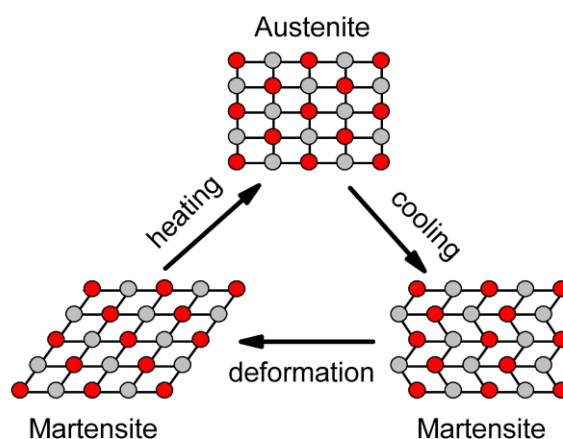


Figure 1. Phase changes associated with the shape memory effects. Mmm-jun, https://commons.wikimedia.org/wiki/File:NiTi_structure_transformation.jpg. Used under CC-BY-SA-3.0.

In the case of superelasticity, an imposed mechanical strain can stimulate the transformation of austenite to martensite, with the associated mechanisms of the transformation accommodating relatively large strains (up to about 8%) compared to what is typical for elastic deformation in metals (up to about 0.5%). If all the deformation imparted in the superelastic temperature range is achieved through martensitic phase transformation, then the original specimen shape can be recovered by removal of the stress. More discussion of superelasticity including some animated examples can be found on a webpage⁸.

We need to note an important difference between superelasticity and shape memory behavior. As we have seen in Figure 1, the latter is observed when subjecting the material to temperature changes. The desired shape memory performance must be imparted by “training” the material, which involves specified temperature modifications and the imposition of a preferred shape within a particular temperature range during that training⁹. As said above, mechanical strain is involved in superelasticity. The common feature of both types of behavior is the martensitic transformations.

These characteristic processes in NiTi alloys are associated with diffusionless phase transformations^{10–12}. The phase change occurs with atoms moving in an organized manner relative to their neighbors. The homogeneous shearing of the parent austenitic phase creates a new crystal structure without any compositional change. Shear transformations occur through the cooperative and systematic motion of all atoms over small distances with respect to their neighbors in the region concerned; the cooperative motion has, in turn, an impact on the macroscopic shape change¹³. Therefore, the macroscopic deformation associated with shape memory and superelasticity is different from shape changes generated by conventional plasticity (i.e. dislocation glide). It is worth emphasizing that the cooperative character of the crystal lattice rearrangement is the particular property that distinguishes martensitic transformations as a separate class of phase transformations.

It is also important to understand that the phase change associated with the shape memory effect is reversible. Therefore, as we will see in the next section, the thermodynamic stability of each phase is important to the performance of SMAs.

Although the shape memory phase change is reversible and superelasticity is an elastic process, the repeated cycling of the structural reactions involves a hysteresis effect. Thus, fatigue still has an impact on SMAs. Functional

fatigue of shape memory alloys leads to changes of physical, mechanical, and shape memory properties; it arises during cyclic thermal or mechanical loading and is due to (irreversible) generation of dislocations in the martensitic phase transformation^{14–17}. Through transmission electron microscopy (TEM) studies on single crystals of NiTi¹⁵ and scanning electron microscopy of Ni-Ti microcrystals¹⁶, the mechanism for the multiplication of dislocations during martensitic transformations has been discovered. Accumulation of defects over time causes internal crack formation and crack propagation, which can lead in many instances to catastrophic failure¹⁴.

There is in Materials Science and Engineering (MSE) the so-called MSE triangle, which has at its vertices structure, interactions, and properties⁵. We have already briefly described above the key macroscopic properties and structure of nitinol. To some degree readers will be acquainted with various aspects of the microscopic structure and properties while perhaps knowing something about the atomic interactions—depending on one’s academic or professional discipline. Familiarizing oneself with aspects of all three vertices *as well as the connections between them* yields practical and useful knowledge and provides a sound basis for instruction. Hence, the ensuing paragraphs of this instructional article, which address all three points and present the story of their relations.

2. THERMODYNAMICS OF SHAPE MEMORY PHASE FORMATION

The formation of different phases in shape memory behavior is explained in terms of thermodynamics. The key property is the Gibbs function (Gibbs energy) defined as

$$G = H - TS \quad (1)$$

where H is the enthalpy, T is thermodynamic temperature, and S is entropy. One of the thermodynamic stability criteria is formulated

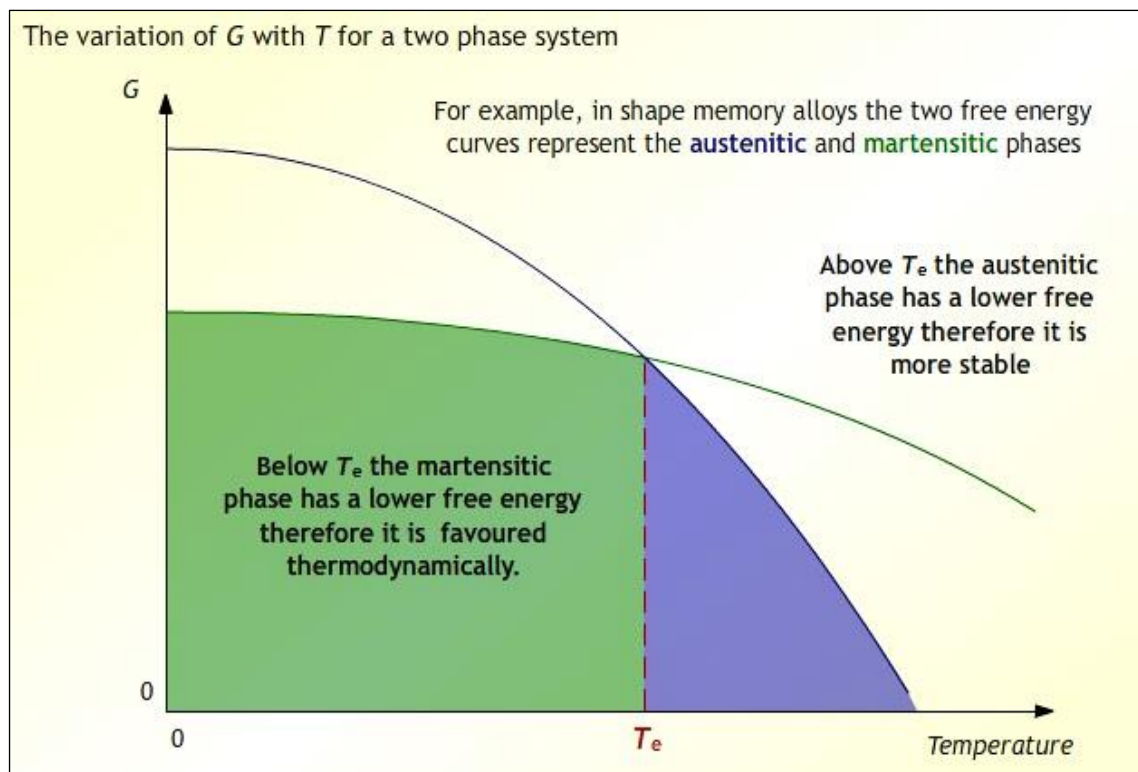


Figure 2. Phase diagram showing variation of the Gibbs function (G) as a function of T for a two phase system, where T_e denotes the phase change temperature. For SMAs, the phase change of interest is a reversible martensitic transformation. The austenitic and martensitic phases of SMAs are phase types and are not equivalent to the crystallographic phases of steel with the same names.

Source: http://www.doitpoms.ac.uk/tlplib/superelasticity/martensitic_basic_thermodynamics.php, CC-SA 2.0

in terms of G , namely⁵, the change of the Gibbs function ΔG . The criterion is that

$$\Delta G < 0 \quad (2)$$

in a natural process. The process can be physical or chemical.

As noted above, SMAs appear in one of two phases, austenite or martensite. Figure 2 shows how the Gibbs function changes for both phases as a function of temperature. For superelastic and shape memory alloys, the austenite phase is stable at higher temperatures and martensite is stable at lower temperatures. Sometimes, the austenitic phase is termed the “parent” phase.

Historically, Wayman around 1983 dealt with calculations of the thermodynamic

forces driving martensitic transformations¹⁸. Following this beginning to the point of discussing the associated changes in morphology, Kashchenko and Chashchina have written in 2013: In regard to the interpretation of the morphological features, the contact between the initial (austenite) and the final (martensite) phase throughout an invariant plane is interpreted as a necessary condition for the minimum of the elastic energy of the coexistent phases to come true¹⁹.

To interpret other aspects of martensitic transitions, the same authors elaborate further on the concept of the Initial Excited State (IES) in the dynamic theory of

martensitic transformations. Kashchenko and Chashchina also suggest that considering the IES concept is necessary to resolving certain problems related to carbon diffusion during transformations in alloyed steel. This provides understanding of growth rates and the spatial scale of changes associated with crystal transformation.

3. A FEW OBSERVATIONS

Many experimental and theoretical studies have explored the strength and fatigue behavior of nitinol in order to uncover ways to improve the mechanical performance of SMAs. Further research work on various point defects such as antisites, exchange of atoms, and vacancies have provided more insight towards understanding the composition and atomic order dependence of NiTi alloy properties.

As already noted near the end of Section 1, with repeated cycling, the increasing number of dislocations generated during the martensitic phase transformation can cause undesirable functional and structural fatigue of NiTi. According to Zarnetta and colleagues¹⁷, those dislocations are closely related to the geometric compatibility at the developing interface between the high-temperature phase (known as B2) and low-temperature phase (known as B19). In other words, to maintain the functional stability of SMAs during consecutive temperature change cycles, thermal hysteresis has to be mitigated. This can be done in specific cases. Zarnetta and coworkers studied Ti-Ni-Cu-Pd alloys, depositing them by a thin-film composition-spread technique. They studied functional stability using differential scanning calorimetry (DSC, see for instance²⁰). They have demonstrated that a specific quaternary bulk alloy $\text{Ti}_{50.2}\text{Ni}_{34.4}\text{Cu}_{12.3}\text{Pd}_{3.1}$ exhibits significantly improved functional stability compared with other SMA compositions.

Other research groups explore different compositions. One such alloy is the Ni_4Ti_3

phase that precipitates in Ni-rich NiTi alloys. It has been studied by first principles quantum mechanics^{12, 21} as well as obtained experimentally²².

4. OVERVIEW OF OBSERVATIONS

An obvious way of affecting the structures of SMAs is the introduction of atoms of other elements. The stability of an interstitial atom in the NiTi phase is assessed based on the so-called solution energy E_s calculated as follows:

$$E_s = E(\text{NiTi} + \text{X}) - [E(\text{NiTi}) + E(\text{X})] \quad (3)$$

$E(\text{NiTi} + \text{X})$ and $E(\text{NiTi})$ are the total energies of the NiTi phase with and without the interstitial defect. The term $E(\text{X})$ represents the energy per atom of the interstitial in its stable form when placed in a large vacuum box. When the values of the solution energy are positive, that means that the respective element is insoluble in NiTi, while negative values account for stable defects. Our inequality (2) pertaining to the Gibbs function is at work again.

Hydrogen, helium and argon have been tried in this context. However, Ar and He interstitials have positive energies of solvation, that is, also positive energies of interstitial formation, while H interstitials have negative energy formation values. Therefore, only H atoms form stable interstitial defects. This has been predicted by quantum-mechanical calculations of Holec and his colleagues¹² as well as experimentally. In the annealing experiments, hydrogen partial pressure could be controlled by mixtures of H with inert gases, but neither Ar nor He is expected to be found in NiTi after annealing^{12, 23}.

There are three non-equivalent interstitial positions in the cubic B2 structure of NiTi¹². They are displayed in Figure 3.

Accepting now the fact that H atoms can penetrate the NiTi lattice and “settle” in interstitial positions, the next logical question

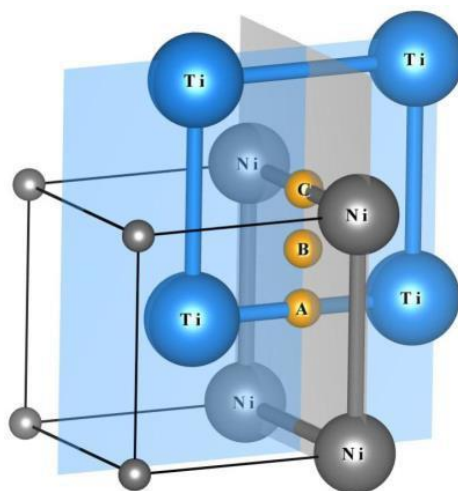


Figure 3. Three nonequivalent interstitial positions in the cubic B2 NiTi lattice. Larger blue spheres are Ti atoms, smaller gray spheres are Ni atoms. The interstitial positions A, B, and C are marked with the small orange spheres. Blue planes contain only Ti atoms while gray planes are occupied by Ni atoms. For the tetrahedral B, the nearest neighbors are 2 Ni and 2 Ti atoms. For the octahedral position A, the surrounding octahedron is formed by 4 Ni and 2 Ti atoms. The octahedral position C is characterized by 2 Ni and 4 Ti nearest neighbors. Source: Reprinted Fig. 1 with permission from D. Holec, M. Friák, A. Dlouhý and J. Neugebauer, “Ab initio study of point defects in NiTi-based alloys, *Physical Review B*, 89(1), 014110 (2014). Copyright (2014) by the American Physical Society.¹²

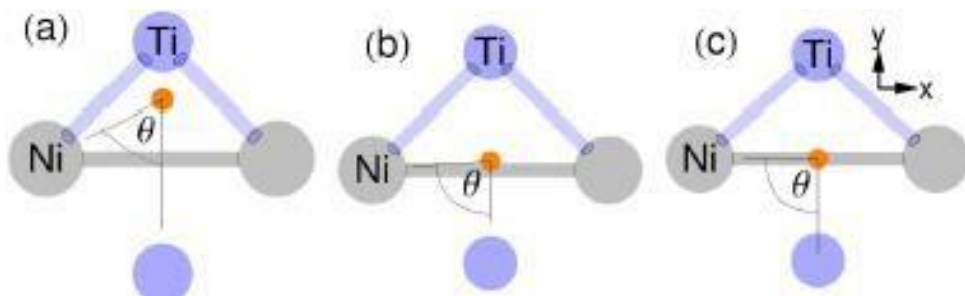


Figure 4. The interstitial atom shown as a small orange sphere in different positions. (a) Starting tetrahedral interstitial position with 2 Ni and 2 Ti atoms as the nearest neighbors relaxes into (b) octahedral-like non-symmetrical environment with 2 Ni and 4 Ti atoms. (c) Octahedral interstitial position with 2 Ni and 4 Ti nearest neighbors. Note that in (b) the interstitial atom is not on the line connecting two Ni atoms while in (c) it is on that line. Source: Reprinted Fig. 3 with permission from D. Holec, M. Friák, A. Dlouhý and J. Neugebauer, “Ab initio study of point defects in NiTi-based alloys”, *Physical Review B*, 89(1), 014110 (2014). Copyright (2014) by the American Physical Society.¹²

is: where do they settle? Figure 4 shows us the scenarios that are possible. Aspects of thermodynamic stability, mentioned earlier, are important. Holec *et al.* state that “even though the tetrahedral site provides an interstitial position with the lowest solution energy as

compared with other two interstitial sites A and C, the ideal geometry shown in Fig. 4a (i.e. the starting configuration for structural relaxation) does not represent a stable configuration for the H atom”¹².

5. CHARACTERISTICS OF SMAs

Drawing from the studies evaluated above, we can identify important characteristic features, behaviors, and performance aspects of NiTi. In order to provide better education on SMAs—including not merely *what it is* but information on all points of the MSE triangle and on the connections between them—we enumerate the relevant details below.

- NiTi shows a reversible martensitic phase transformation and a shape memory effect.
- The associated distortions of the lattice can be quantified by analyzing the geometry of structural parameters which are related to the solution energy per atom.
- The detailed analysis of the geometries helps to reveal the position change of interstitials. The lowest solution energy of an interstitial position of tetrahedral site B does not represent a stable configuration for the H atom; the position with the lowest solution energy moves further apart and reaches to the less symmetric interstitial site.
- He and Ar atoms are not able to form stable interstitial defects. Ar and He have lower solubility in Ni + Ti alloys because of the larger atomic sizes. As noted by Holec and his colleagues¹², a He atom has the radius of 128 pm, an Ar atom 174 pm. This is “no competition” for H with its atomic radius of 53 pm = 0.053 nm.
- As a consequence of that size difference, hydrogen atoms tend to form stable interstitial defects. The defects greatly influence the martensitic phase transformation in NiTi alloys by altering the mutual thermodynamic stability of the high-temperature cubic and the low temperature less-symmetric phase of NiTi in terms of interstitial solutes. The temperature of the martensitic transformation depends significantly on the composition, including the presence and concentration of H interstitials. Therefore,

it is possible to control H partial pressure in the martensitic transformations by mixing hydrogen and inert gases in annealing experiments; we know that the inert gas atoms will not remain in the alloy...

6. APPLICATIONS OF SMAs

Applications of SMAs are numerous and various. A SMA spoon will bend itself when put into a warm tea or coffee. A magician can do this, claiming that the bending occurs because of domination of his spirit over inanimate matter. SMA actuators, subjected to thermomechanical cycling under external load over the transformation range, are expected to survive millions of cycles²⁴; an actuator is responsible for controlling or moving a system or a mechanism. Other applications include: highly resilient eyeglasses frames; temperature control systems, including fire security systems; helicopter blades; retractable antennas in cell phones.

A separate area of applications is medicine. Nitinol has been used as small wires to mark breast tumor locations; the surgery can then be performed in a more accurate way. However, Ni should not come in direct contact with human body parts because Ni is toxic and its release rate into the surroundings varies over a wide range and has been reported to increase with time²⁵. Therefore, methods of covering Nitinol with titanium nitride barriers have been developed, notably by Elazar Gutmanas and Irina Gotman^{26–29}.

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