Chapter 1

Some General Points about SMAs

1.1. Introduction

What are these alloys that we call “shape-memory alloys”?

To begin with, they are metallic alloys with two, three or even four components, with very special compositions.

There are two main families of SMAs:

– “copper-based” materials – Cu-Al (Zn, Ni, Be, etc.);
– nickel-titanium-X materials (where X is an element present in small proportions) – NiTi (Fe, Cu, Co, etc.).

These materials are called “memory” materials, meaning that they have the property of “remembering” thermomechanical treatments to which they have been subjected (traction, torsion, flexion, etc.).

Specifically, the geometric shape that they had, at high and low temperatures, constitute two states which they “remember”. This memory is developed by way of training – i.e. often by the repetition of the same thermodynamic loading: this is in terms of stress or strain imposed and/or in terms of temperature.

The physical key to “shape memory” lies in a phase transformation between a parent phase called austenite (A) and a produced phase called martensite (M). For SMAs, this phase transformation is described as thermoelastic. It involves a change of crystalline lattice between the phase A, also known as the “high temperature” phase,
and a phase M, also known as the “low temperature” phase. This change is called a “martensitic transformation”. The austenite is transformed into “martensite variants” (a term which will be explained later on).

As shown by the photographs taken by Chu and James [CHU 93] of “copper-based SMAs”, the microstructure may prove very complex, which makes it difficult to analyze them (Figures 1.1 to 1.4).

![Figure 1.1. Optical micrograph of a microstructure of a Cu-Al-Ni alloy: a “complex lattice”; horizontal extent 0.75 mm: reproduced with kind permission from C. Chu and R.D. James [BHA 03]](image)

1.2. Why are SMAs of interest for industry?

SMAs belong to the category of so-called “adaptive” materials. Not only are they useful as structural elements, appreciable for their mechanical properties such as toughness; they are also capable of fulfilling functions such as that of a sensor or an actuator.

They are very widely used in domains with high financial added value – for example:

– the biomedical industry: used for implants, prostheses or stents, which are “latticed” tubes that are inserted into a conduit – e.g. a bronchus;
– aeronautics: filtering out of harmful frequencies, noise reduction (Boeing);
– aerospace: deployment of antennas;
– watch-making: insertion of an SMA spring into the mechanism of a watch;
– the nuclear industry: for pipes.
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Figure 1.2. Optical micrograph of a microstructure of a Cu-Al-Ni alloy: a “corner”-type microstructure; horizontal extent 0.75 mm: reproduced with kind permission from C. Chu and R.D. James [BHA 03]

Figure 1.3. Optical micrograph of a microstructure of a Cu-Al-Ni alloy: “cross-twinning”; horizontal extent 0.75 mm: reproduced with kind permission from C. Chu and R.D. James [BHA 03]
However, the cost of the alloy has hitherto been a serious hindrance for potential applications in the automobile industry, because of the tight budget in terms of mechanical parts in this sector.

Indeed, this cost is very heavily dependent on the delivery state, i.e. on the metallurgic treatment, shaping and geometry of the manufactured parts.

For instance, according to information provided by Nimsis-Technologies:

– a polycrystalline Cu-Al-Be alloy, in the raw spun state, costs around $390 per kilogram. If it is trained, the cost of a spring made of the same alloy may run to dozens of dollars;

– a round nickel-titanium wire 1, 2 or 3 mm in diameter sells for between $190 and $450 per kilogram; thin bands between $1300 and $1950, and a stent around $13.

At present, in France, there are three companies which supply SMAs:

– “Mmomtal technologies”. Bought on 6 July 2011 by Stryker, one of the world leaders in the domain of orthopedics and medical devices, Mmomtal is a specialist in the production of implants and prostheses made of nitinol, and generally everything from the choice of alloy to the design of the parts. This entails possible training
of the components, including the different stages of transformation (wire-drawing, metal-shaving, and shaping of the parts);

– “NiTiFrance”. This company has been in existence since 1998. It is a branch of the biomedical group Lpine. It has a market presence in the United States as “Nitinol Devices and Components” and specializes primarily in osteosynthesis staples.

Mmomtal produces its alloys using the “hot crucible” technique, which is excellent for obtaining homogeneity in the resulting composition, but causes the problem of excessive oxygen absorption. NiTiFrance uses a “cold copper crucible”, which increases the ductility of the alloy (by 15 to 30% between the two solutions) by decreasing the percentage of oxygen absorbed. Remember that titanium is highly oxyphilic, and that oxygen tends to position itself in the interstitial site in crystalline lattices, which causes an increase in the fragility of the material.

As regards the activity of Nimésis-Technologies, it covers the main sectors of applications for SMAs, satisfying the demand for sensors and actuators.

Founded a century ago in Besanon, the company “MICRO-MEGA” is an uncontested leader in endodontics. In October 2009, it was bought by a German industrial dentistry corporation. It has developed a profitable niche market in NiTi “nerve lag” for root-canal work. It is the pseudo-elasticity of the alloy which is exploited here (see Chapter 2).

One of the drawbacks to these alloys is that they have a relatively slow dynamic of use, due to the prolonged period of heat transfer. However, the use of thin films can greatly improve the situation. An operational frequency of 100 Hz has been obtained by exploiting the austenite to R phase transformation for certain NiTi based alloys [TOM 06].

With massive SMAs, even a slow dynamic does not prevent their use in development of actuators.

The specific uses of SMAs, relating to their particular properties associated with phase transformation, will be discussed in detail in Chapter 2, entitled “The world of SMAs”.

1.3. Crystallographic theory of martensitic transformation

Let us first examine the crystallographic aspect of martensitic transformation. At a low temperature, the phase M (hereafter called $M_T$ – self-accommodating martensite) obtained from A by simple cooling of the alloy and therefore isotropic redistribution
of the variants, may, under external stresses, produce major deformations associated with the reorientation of the martensite variants. This associated behavior is qualified as “pseudo-plastic” (Figure 1.5).

“Shape memory” constitutes a particular manifestation of crystalline phase transformation, known as “martensitic phase transformation”. This is a solid-to-solid phase transformation where the parameters of the crystalline lattice change suddenly (e.g. \( A \to M \) when cooled) at a specific temperature of the alloy in question. Although the change is abrupt and the distortion of the lattice is very significant, there is no diffusion and no alteration in the relative positions of the atoms during the transformation. This transformation is said to be “displacive”, of the first order (sudden change in the crystalline parameters) (see Figure 1.6).

If the alloy is heated, it undergoes thermal expansion until the reverse transformation (\( M \to A \)) occurs at another critical temperature. The difference between the two critical temperatures (\( A \to M \)) and (\( M \to A \)) shows that the behavior of SMAs is hysteretic. The conventional SMAs exhibit a small amount of hysteresis.
Figure 1.7 illustrates the so-called “pseudo-elastic” traction curve representing a phase transformation under stress.

One observable characteristic of martensitic transformation is the microstructure that it causes. In a typical transformation, the austenite, which is often “cubic” has a greater degree of symmetry than the produced phase. This is shown diagrammatically in two-dimensions in Figure 1.6, where the austenite is a square (a) and the martensite a rectangle (b and c). Consequently, we have multiple martensite variants – in this case two: (b and c). The number $\nu$ of variants obtained depends on the change in symmetry during the transformation.

More specifically:

$$\nu = \frac{\text{number of rotations in } P_a}{\text{number of rotations in } P_m}$$

where $P_a$ ($P_m$) is the symmetry group of A(M).

Indeed, there is no reason why the austenite crystal should transform into only one martensite variant. However, the microstructure must be consistent and may be presented in the architecture shown in Figure 1.6 (d), which is corroborated by transmission electron microscope (TEM) observations of a nickel-aluminum alloy (see the images of microstructures in Figures 1.1 to 1.4 [BHA 03]).

This need of the crystals to form mixtures of variants, while the whole must remain consistent, gives rise to complex structures which we refer to as the microstructure of the martensite.
1.4. Content of this book

1.4.1. State of the art in the domain and main publications

The first widely-recognized work in French on the topic was a basic introduction to SMAs, by Patoor and Berveiller [PAT 90]. Their second book was more significant in terms of the mechanical behavior of these alloys [PAT 94].

The question of the microstructure of martensite: “why it forms and how it gives rise to the shape-memory effect” constitutes the premise of the book with the same name by Bhattacharya [BHA 03]. The first founding theorems in this theory can be attributed to Ball and James [BAL 87], [BAL 92]. The chapter on martensitic transformation (Chapter 3) will make use of their proposals about the mathematic description of the microstructure.

Wayman’s book [WAY 64] is largely used as an introduction to crystallography of martensitic transformation (CMT).

With regard to the book by Khachaturyan [KHA 83] and the review by Roytburd [ROY 78], they predate the discipline of CMT (by linear or nonlinear construction) and deal with linear geometric theory.

The monograph published by Abeyaratne and Knowles [ABE 04] consists of an introduction to the dynamics of phase transformations.

The reader will find fairly general information about SMAs and their use in Shape Memory Alloys, the book written by Japanese scientists such as Shimizu, Tadaki, Homma, Miyazaki, Otsuka, Suzuki and Sekiguchi, translated into English [FUN 87].

Structural calculations about SMAs can be found in a special edition of the Revue des lments finis (Finite Element Journal) [REF 98].

Finally, Smith [SMI 05] extended his study to intelligent systems such as ferroelectrics, ferromagnetics and of course, SMAs.

Note that these materials are not intrinsically intelligent; rather it is the usage that is made of them that can be intelligent (or not)! Also, the title Journal of Intelligent Materials and Structures may be considered to be ambiguous.

1.4.2. Content of this book

This chapter is an attempt to place shape-memory alloys in the context of physics and the mechanics of materials and to set out the key physical concepts of martensitic transformation and reorientation of martensite plates.
Chapter 2 contains a few elements on the basic metallurgy of SMAs, written by Michel Morin (MATEIS (Materials, Engineering and Science) lab at INSA in Lyon). Particular attention is paid to phase diagrams and *ad hoc* thermal treatments, drawing the distinction between copper-based SMAs and NiTi materials and their derivatives. The chapter closes with a description of the functional properties of SMAs (simple memory effect, pseudo-elasticity, recovering stress and training).

Chapter 3 borrows heavily from Kaushik Bhattacharya’s book, *Microstructure of martensite: why it forms and how it gives rise to the shape-memory effect* [BHA 03]. Following an overview of continuum mechanics, the kinematic (or Hadamard) compatibility conditions are examined, as well as the twinning equation between two martensite variants and special microstructures.

Chapter 4 defines the thermodynamic framework used for the modeling of the materials, referred to as generalized standards [HAL 75].

Chapter 5 touches on the earliest applications of the crystallographic theory of martensite on SMA monocrystals.

Chapter 6 also borrows from Chapter 5 (*Model development for shape memory alloys*) of Ralph Smith’s book *Smart Material Systems: Model Development* [SMI 05].

It consists of the description of the “all-or-nothing” Preisach models, Falk’s investigations into the deformation potential, the statistical approaches of Seelecke and Muller and Smith’s extensions of these.

Chapter 7 introduces three macroscopic models with internal variables: namely, those advanced by Raniecki and Lexcellent, referred to as the $R_L$ models; the Metz-Nancy approaches, which are more concerned with the microstructure [CHE 11]; and finally the more mathematical models put forward by Kelly and Bhattacharya [KEL 12]. An elastohysteresis model was also described [FAV 88].

In Chapter 8, “material strength”-type calculations are performed on beams in flexion or torsion and a number of distilled exercises.

Chapter 9 will examine the behavior of magnetic shape-memory alloys.

In Chapter 10, some elements of the fracture mechanics of SMAs will be set out.

A general conclusion will focus on the numerous problems which still need to be resolved in this domain of functional materials.

Although there is a common thread running throughout the book, the author has been careful to make sure that each chapter can be read independently of the others. For instance, a reader interested in metallurgy can focus on Chapter 2 and on Chapter 9 about magnetic shape-memory alloys.