Thermal and Thermomechanical Cycling Studies of Nickel-Based Shape Memory Alloys for Engineering and Medical Applications

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Abstract: Shape memory materials (SMAs) are those that can return to their initial shape after deformation under a stimulus, such as temperature or stress. SMAs are capable of recovering deformations of up to 8%. Generally, the martensitic transformation is reversible nature and the SMAs exhibit two unique characteristics, superelasticity effect (SE) and shape memory effect (SME), depending on whether these properties/responses are brought on by stress or temperature, respectively. Since the SMAs undergo full cycling, they transform from austenite to martensite at temperatures between Mf and Af. However, partial cycling refers to heating above As but below Af followed by cooling to below Mf. The phase transformation is partial before it is complete, consequently, only a smaller amounts of the phases are subjected to phase transition. Based on the operating temperature window and the transformation temperatures of the alloy, partial cycling can be divided into three categories. This chapter discusses the various types of partial cycling and the behavior of NiTi-based SMAs during cycling.

Keywords: Shape memory alloys, partial transformation, transformation temperatures, austenite and martensite.

Introduction

Shape memory effect was first discovered in 1931 by A. Olandar in a AuCd alloy and reported the phenomenon that was observed as a rubber-like behaviour [1]. After almost a decade, the metastable β-based Cu-Zn shape memory alloy was discovered by A.B. Greninger and V.G.Mooradian [2], and the concept of thermoelastic martensite was then proposed by Kurdjumov in 1949 to explain the reversible nature of CuAl and CuZn alloys [3]. The term shape memory effect was coined by Chang and Read in 1951 to describe the thermoelastic behaviour of SMAs [4]. Nevertheless, none of them made any inroads into the commercial market until 1963 when Buehler W.J. and his co-workers from the Naval Ordnance Laboratory in the U.S. discovered the NiTi shape memory alloy, which is now commercially known as Nitinol [5].

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Currently, SMAs are widely used in many industries, including automobile, aerospace, aviation, robotics, biomedical, textile and garment, defence, and electrical and electronics. Recently, NASA has developed a smart wheel based on Ni-rich NiTi SMA for the interplanetary and lunar exploration purposes [6]. It is forecast that by 2023, the global market for shape memory alloys will surpass USD 20 billion.[7]. Till date, a number of shape memory alloy systems that exhibit shape memory characteristics have been discovered and developed, and some of them are listed in Table 1.

Table 1: Popular alloy systems exhibiting shape memory characteristics (Mohd Jani et al., 2014; Wayman, 1993)

Alloy systems	Alloy composition
Ni-Ti	NiTi, NiTiCu, NiTiNb, NiTiFe, NiTiCo, NiTiPt, NiTiPd, NiTiHf, NiTiZr
Copper	CuZn, CuSn, CuZnAl, CuAlNi, CuAlBe
Iron	FePt, FePd, FeMnSi, FeNiC
Titanium	TiTa, TiNb, TiMo, TiTaAl, TiTaSn, TiTaSi
Others	ZrCu, ZrCuNiCo, AuCd, AgCd, CoNiAl, CoNiGa, NiMnGa, InTl, NiAl, InCd, RuTa, RuNb, AuTi, MnCu,

The following are the characteristics that are significant in the context of SMAs;

a) Phase transformation temperatures (A_s, A_f, M_s, M_f);
b) Recovery strain;
c) Recovery stress; and
d) Hysteresis

a) Phase Transformation Temperatures

When the SMAs are cooled down from the austenitic phase, they undergo the thermoelastic martensite transformation over a range of temperatures. The temperatures at which the martensitic transformation start and finish are referred to as M_s and M_f temperatures, respectively. Similarly, A_f and A_s temperatures refer to the temperatures at which the austenite transformation begins and ends, respectively, during heating. The intermediate phases, including R-phase, may also be present in the material depending on the alloy system, thermomechanical treatment, etc. When this phase forms, the corresponding transformation temperatures can be referred to as R_s and R_f, respectively.

There are a number of factors that affect the transformation temperatures of shape memory alloys, for example, the alloy composition, microstructure, degree of order, thermal and thermomechanical treatments, as well as the defect density (dislocations and point defects) [8]. The traditional techniques to determine the transformation temperatures of SMAs include differential scanning calorimetry (DSC) and electrical resistivity (ER). Other techniques, including dynamic mechanical analyzer (DMA) [9] and dilatometry analysis [10], are also employed to determine the transformation temperatures.

b) Recovery Strain

Upon heating above As temperature, it is possible to recover some of the strain imparted during the deformation of an SMA in the martensitic state (up to 8%). Various factors influence the magnitude of recovery strain, for instance alloy chemistry, thermal and mechanical processing, stress, and working temperature. A range of testing methods can be used to measure the recovery strain, such as dynamic mechanical analyzer, bend recovery test, and thermomechanical cycling test. The thermomechanical cycling test (thermal cycling under constant stress) is the most common method for determining recovery strain. The magnitude of the recovery strain can be determined by comparing the maximum and minimum strains found on the strain versus temperature plot.

Recovery Stress

The recovery stress is generated by elastic recovery stress during deformation. The SMAs on deformation generate stresses, which are stored in the martensitic variants during the deformation, on heating above A_s temperature under a constraint. It can be used to provide support or external confinement for mechanical and civil structures.

Hysteresis

Hysteresis occurs when the forward and reverse transformation trajectories do not coincide during cooling and heating (thermal hysteresis) or loading and unloading (stress hysteresis). The incompatibility of the interface between the transforming phases acts as an energy barrier for the transformation and causes hysteresis [11,12]. The geometrical non-linear theory states that the second eigenvalue of the transformation strain matrix should have the value of one in order to reduce the energy associated with the interface between the martensite and austenite phases. Hysteresis results when there is a difference between forward and reverse transformation paths as a result of deviation from this condition [13–15]. The area enclosed by the forward and reverse transformations (hysteresis loop) represents the energy loss during the phase transition.

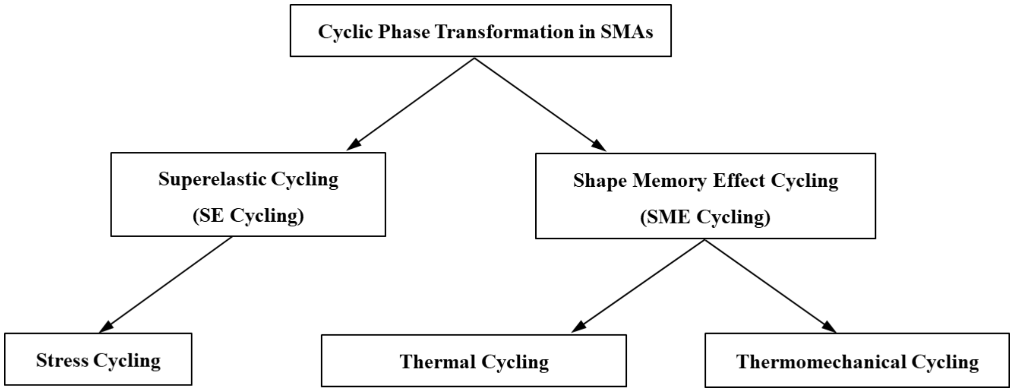

Figure 1: Classification of cyclic phase transformation in shape memory alloys (Van Humbeeck, 1991).

SMAs undergo repeated cycling between their phase transformation temperatures, resulting in functional fatigue, which impacts properties including transformation temperatures, recovery strain, recovery stress, and hysteresis width. [16]. In 2004, Eggeler et al. coined the term functional fatigue and it can also be referred to as cyclic fatigue, phase transformation fatigue, and actuation fatigue [17–19]. In contrast to structural fatigue, which occurs because of cyclic loading-unloading, cycling occurs when the austenite and martensite phases go through repeated phase transformations (i.e., austenite and martensite).

The studies on fatigue behaviour of NiTi SMAs were initiated in the late 1970s. Melton K.N. first studied the mechanical fatigue behaviour of binary NiTi with varying M_s temperatures. The NiTi SMA showed an increased fatigue life with decreased M_s temperature and vice versa [20]. Miyazaki et al. pioneered the study of the thermal cycling behaviour of NiTi-based SMAs in 1986 [21]. Later, this field attracted the shape memory alloys research community as this area is very much essential from an application point of view. An overview of the effects of stress, thermal, and thermomechanical cycling on shape memory alloys was presented by J. Van Humbeeck. Depending on the type of stimulus and the nature of phase transformation, cyclic phase transformations can lead to either be superelastic effect (load-dependent) or shape memory effect (temperature-dependent). There are two types of shape memory cycling: thermal (stress-free) and thermomechanical (thermal cycling under constant load), as shown in **Figure**

1. Several factors influence the functional fatigue behaviour of SMAs, including internal factors (alloy system, composition, crystal structure, compatibility with transforming phases) and external factors (applied stresses, temperature ranges, training methods, and training cycles) [22].

Partial Cycling of SMAs

Full cycling is generally referred to as cycling, and partial cycling is defined by the working temperature range based on phase transition temperatures. The SMAs undergo full cycling when they change from 100% martensite to 100% austenite. Basically, the cycling temperature varies between M_f and A_f. SMAs undergo a full cycle when they change from martensite to austenite. Basically, the cycling temperature varies between M_f and A_f. As a result of incomplete cycling, only a part of the phases will be subjected to phase transition before the stimulus (temperature or stress) ceases [23]. As shown in **Figure** 2, there are three types of partial cycling, depending on the upper and lower cycle temperatures.

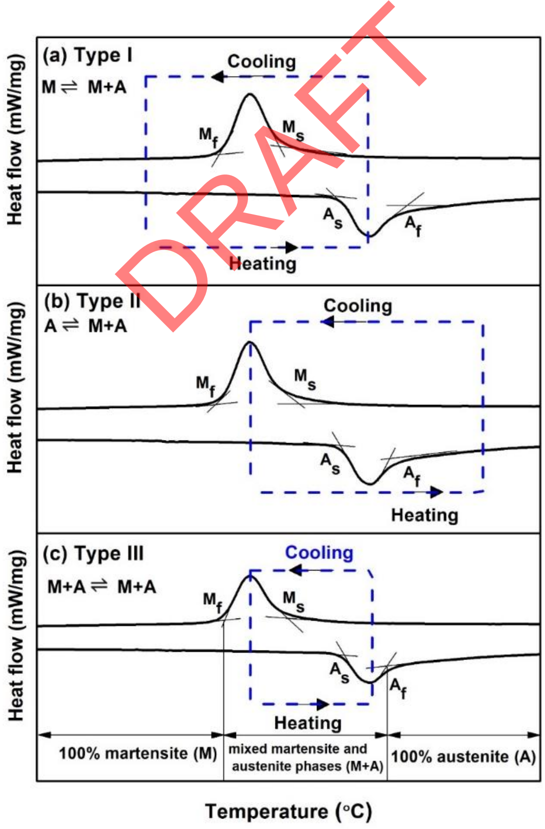

Figure 2: Three different types of partial thermal cycling in SMAs

In Cu-based SMAs, partial/incomplete cycling studies show a decrease in the volume fraction of transforming masses [24] and an increase with NiTi-based SMAs. Furthermore, it affects the temperature at which the transformation occurs [23]. When the upper cycle temperature changes slightly, the volume fraction and density of dislocations in SMAs change as well (28). In addition to the degree of order, incomplete cycling also affects the hysteresis behavior of SMAs. Partial cycling causes changes in dislocation structure, elastic energy stored, and interface interactions [27]. Studies regarding partial thermomechanical cycling have found that controlled transformation strain by partial transformation increases the lifespan of an SMA by ten times. It has been suggested that incomplete cycling can improve the fatigue life of SMA actuators [28].

The NiTi SMA was subjected to cycling between -50 °C (below Mf) and 75 °C (between As and Af) for 20 cycles during Type I partial thermal cycling. The transformation temperatures for Type I partial cycling decrease with increasing cycles just as they do for full cycling. Partial cycling of Type I reduces temperatures less than full cycling, as depicted in **Figure** 3.The reason for this is that during Type I partial cycling, austenite is partially transformed into martensite, [29,30], resulting in a lesser number of dislocations during the forward transformation than during full cycling, causing a lower dislocation density. In addition, Type I cycling does not result in the occurrence of an intermediate R phase even after 20 cycles.

As depicted in **Figure** 3, Type II partial thermal cycling was performed on NiTi SMA between $M_s<T_{min}<M_f$ and $T_{max}>A_f$. Type II partial cycling results in a much lower reduction in martensite start (M_s) temperature than Type I partial cycling or full cycling. As cycling continuous, the area corresponding to the martensite transformation curve shrinks. Ms temperature decreases during cooling, resulting in a decrease in transformation volume. It takes about ten cycles for austenite to reach its saturation temperature (A_f), while its starting temperature (A_s) stays relatively constant.

Figure 3 shows a partial thermal cycling of Type III on NiTi SMA between M_s and A_f temperatures. The alloy undergoes similar transformations to Type II partial cycling when heated under Type III partial cycling conditions. There is a marginal difference between Type II and Type III cycling in terms of the rate of conversion of R phase to austenite and that of martensite to austenite. During cycling, the material undergoes forward and reverse transformations in a smaller volume due to the narrow temperature range.

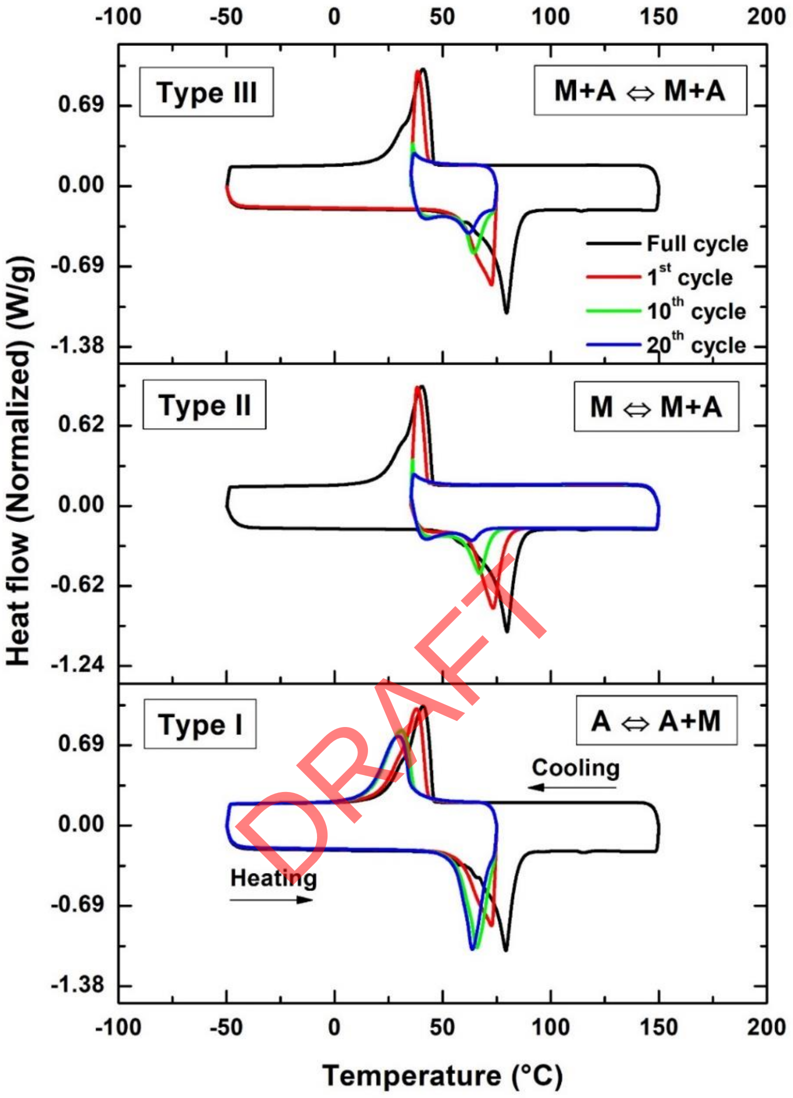

Figure 3: Effect of partial transformation cycling on the shape memory behaviour of NiTi-SMA

Concluding remarks

Partial transformation cycling increases NiTi SMA thermal cycling stability over full transformation cycling. Additionally, partial cycling influencing the formation of intermediate phases. During heating and cooling, Type I partial transformation cycling completely eliminates the intermediate phase. In contrast, when Type III and Type II partial cycling are adopted, intermediate phase formation is promoted.

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