

## Hysteresis in NiTi alloys

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**Abstract.** Large changes in hysteresis are reported as a function of applied stress under thermal cycling experiments in NiTi single crystals. In the low Ni alloy the thermal hysteresis expanded with increasing stress while in the high Ni alloy the thermal hysteresis contracted with increasing stress. The results in both cases meet the limit obtained from Differential Scanning Calorimetry at zero stress. The changes are attributed to the relaxation of elastic stored energy which is primarily due to dislocations emanating at martensite/austenite interfaces. Modifications in thermodynamics formulation are proposed to account for the change in hysteresis via change in the elastic stored energy. Memory effects due to dislocation arrangements imposed under high stress thermal cycles on subsequent thermal hysteresis under low stresses were found to be significant, while variations in thermal hysteresis from cycle to cycle under constant stress are noted to be rather small.

### 1. INTRODUCTION

The stress and thermal induced phase transformations in shape memory alloys are considered thermoelastic at the macroscale with underlying irreversibilities at the microscale producing thermal hysteresis. The thermal hysteresis in shape memory materials is defined as the difference between the forward (austenite(A)-> martensite(M)) and reverse (M->A) transformation temperatures. Thermal hysteresis (under constant stress) is due to reverse transformation at a higher temperature than the forward transformation. Differential Scanning Calorimetry measurements provide the transformation temperatures and thermal hysteresis under no external loading. Upon application of external stress, we postulate that the transformation hysteresis is altered because of relaxation mechanisms such as local plastic deformation near austenite/ martensite interfaces, and change in elastic storage mechanisms such as detwinning of the martensite into a single variant. The role of stress is the current emphasis in this work. Another origin of the dissipative terms during phase transformations, and one that operates even in the absence of stress, are the friction stresses required to move the transformation interfaces. However, this mechanism is not expected to produce asymmetry between forward and reverse transformations.

The purpose of this paper is to demonstrate experimentally the large variation in thermal hysteresis with external stress under thermal cycling conditions. The results meet the differential scanning calorimetry results in the limit of zero stress. The results are reported for 50.1%Ni (at.) and 51.5%Ni NiTi alloys in the aged conditions. We make the important observation that the thermal hysteresis grows with increasing stress in the 50.1%Ni case, while it contracts in the 51.5%Ni case. Although we report only on thermal induced transformations in this paper, an equivalent behavior has been observed for the stress-induced transformation under constant temperatures. Experiments are repeated on several crystal orientations with consistent results, with the current emphasis in this paper on the [111] case.

There has been previous observations and viewpoints on the underlying factors responsible for hysteresis in shape memory alloys [1–3]. The origin of the hysteresis can be attributed to interfacial energy, elastic misfit of phases and variants, however, it has not been made clear how these physical processes change with stress or temperature. The currently proposed continuum models account for hysteresis by using a different critical driving force for the onset of forward and reverse transformation [4, 5]. Further improvements are needed to address irreversibilities in continuum models. The composition of the material, the prior cold work, the heat treatments (resulting in precipitates), and the texture influence the hysteresis as they all alter these dissipative processes [6, 7]. Among these factors, large amounts of cold work is embedded in most cold rolled bars. Therefore, our aim has been to focus on cast single crystals to eliminate grain size and prior cold work effects. We have conducted transmission electron microscopy observations to interpret the underlying dislocation arrangements in our experiments.

## 2. EXPERIMENTS

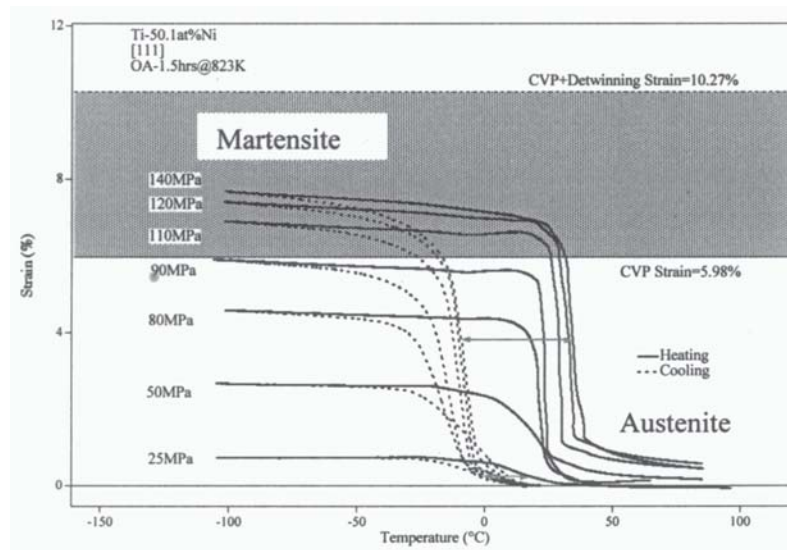
The two materials considered in this work are binary nickel-titanium alloys with 50.1%Ni and 51.5%Ni compositions respectively. These two compositions represents high and low ductility extremes for nickel-titanium alloys. After casting in vacuum, the ingots are grown into single crystals with selected orientations. The single crystals are solutionized and quenched before the experiments. The specimens are aged at 823K for 1.5 hours. This aging process occurs at a considerably higher temperature than the transformation temperatures. The experiments are conducted at constant tensile stress while the temperature is cycled. The strain is measured with a miniature extensometer. The temperature is increased with induction heating and the specimen is cooled with copper tubing with flowing liquid nitrogen. Thermocouples attached to the specimen measure the temperature.

When the specimens are heated and cooled between 100 °C to –100 °C under stress-free conditions the strains produced are nearly zero due to self accommodation of the martensite. We demonstrate the results for the [111] orientation, 50.1%Ni alloy in the aged condition in Figure 1. In Figure 1, the strain temperature curves are shown for constant stress levels of 25, 50, 80, 90, 110, 120 and 140 MPa respectively. The thermal hysteresis is determined by measuring the width of the loop corresponding to one half the transformation strain.

Because the curves are highly nonlinear defining hysteresis at the midpoint of the loops is most meaningful. The horizontal arrows in Figure 1 mark the thermal hysteresis measured at a stress of 25 MPa and 140 MPa respectively. We note that the thermal hysteresis at 25 MPa and 140 MPa were 17 °C and 40 °C respectively, in agreement with the thermal hysteresis value of 17 °C from DSC measurements.

We note in Figure 1 that the shape of the heating and cooling curves are not mirror images marking an underlying difference between the energy requirements for forward and reverse transformation behavior. Specifically, the tails of the strain temperature curves are extended for the forward transformation case compared to the more abrupt reverse transformation behavior. The theoretical predictions of the CVP formation strain and the additional detwinning associated with the coalescence of the variants to a single variant are noted in Figure 1 [6]. At stress levels exceeding 90 MPa, the strains associated with detwinning become substantial. We note that the maximum strain levels fall short of the theoretical values.

In Figure 2 the transmission electron microscopy results are shown for the 50.1%Ni [111] single crystal subjected to the thermal cycling experiments given in Figure 1. We note that the martensite plate is internally twinned and considerable dislocation activity is observed at the martensite/austenite interface. We also note the presence of dislocations in the austenite domains. It is interesting to note the presence of residual martensite, localized slip at transforming interfaces and distributed slip over homogenized regions partially explaining the inability to reach theoretical transformation strains. However, the presence of high dislocation density was not detected in the case of 51.5%Ni crystals. Despite



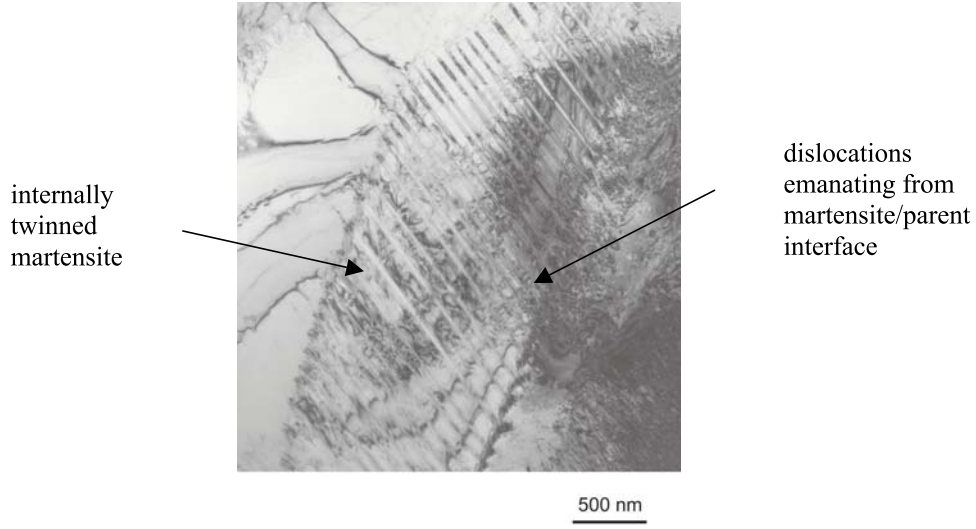
**Figure 1.** Strain temperature response of 50.1%Ni NiTi alloy under constant stresses. The results demonstrate that the thermal hysteresis is not constant and increases with increasing stress levels. The horizontal arrows indicate the thermal hysteresis measured at low stress and high stress respectively.

the higher slip resistance, the 51.5% Ni has a large volume fraction of precipitates, regions which limit the volume available for transformation.

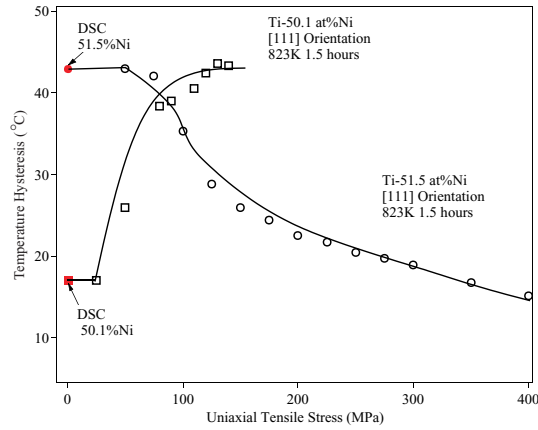
A summary of the thermal hysteresis results are shown in Figure 3 for the 50.1%Ni and 51.5%Ni materials. The thermal hysteresis obtained from DSC experiments are also shown with arrows. With increasing applied stress levels the temperature hysteresis grows drastically for the 50.1%Ni case before reaching steady state levels. For the 51.5%Ni material the thermal hysteresis narrows over a wide stress range. For both materials, the temperature hysteresis data coincide with the differential scanning calorimetry results of 17°C for the 50.1%Ni case and 43°C for the 51.5%Ni case. We note that the main difference between the two materials is their nickel content which translates to differing strengths, i.e. slip resistance, of the austenite domains.

We note that the experimental results obtained here are independent of the number of cycles applied at a constant stress. To minimize stress history effects, the experiments were conducted starting with small stress levels and the stress level was gradually increased until the reversibility of transformation was no longer observed or the specimen fractured. In several cases the experiments were repeated under the same stress level to ensure consistency of results from cycle to cycle. The same specimen was subjected to four repeated cycles in Figure 4 starting with 100MPa. We note that the hysteresis corresponding to first and second cycles are nearly the same for both the 100 MPa and 110 MPa cases. These results make clear that the first cycle results serve as a good description of the response at the corresponding stress level.

One set of experiments was conducted to check the role of prior thermal cycling at high stresses (140 MPa) on the subsequent thermal cycling results at low stresses. The results are given in Figure 4(b) for the 50.1%Ni case. Because the high stress levels dictate the underlying dislocation arrangement, the subsequent hysteresis at low stress levels was considerably elevated. This represents a case where the state variables underlying the deformation have not returned to their original value and the thermodynamic state is altered. Any modeling efforts should address such memory of high stress history.



**Figure 2.** Transmission electron microscopy image from a 50.1%Ni NiTi single crystals that has been subjected to thermal cycling under constant stress. The internally twinned martensite is shown with dislocations emanating from the martensite interface (on the right hand side).



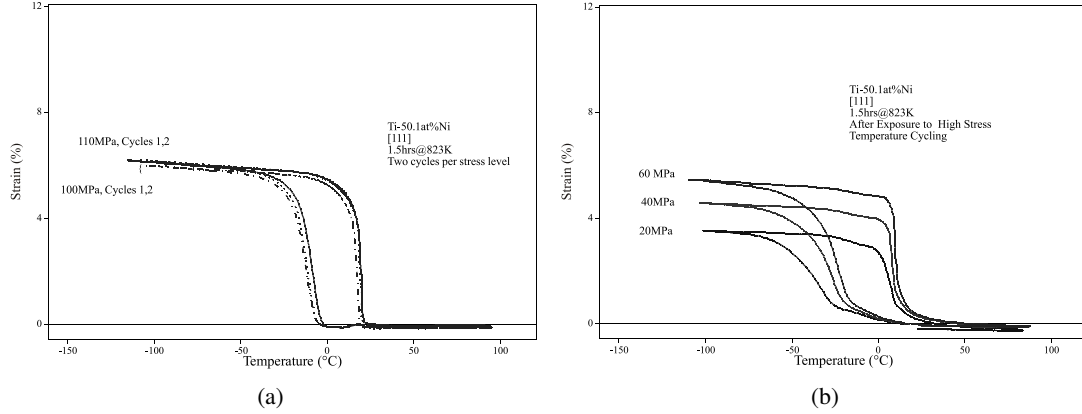
**Figure 3.** The variation of thermal hysteresis with applied stress for the case of two nickel-titanium alloys, one with low and the other with high Ni content.

### 3. IMPLICATIONS OF THE RESULTS FOR MODELING

The thermodynamics of diffusionless martensitic transformation has been expressed in terms of the following energies based on the work of Patoor et al. [4, 8]

$$\Psi(\Sigma_{ij}, T, f^n) = B(T_o - T) \sum_n f^n + \frac{1}{2} \Sigma_{ij} C_{ijkl} \Sigma_{kl} + \Sigma_{ij} \sum_n \varepsilon_{ij}^n f^n + \frac{1}{2V} \int_{\Omega} \sigma_{ij}^{dist} \varepsilon_{ij}^{dist-tr} dV \quad (1)$$

where the first term represents the chemical free energy change, the second term is the overall strain energy stored in the system based on applied stresses, the third term represents the interaction energy



**Figure 4.** (a) Strain temperature cycling (2 cycles at 100 MPa followed by 2 cycles at 110 MPa). The results demonstrate that thermal hysteresis levels do not change from cycle to cycle, (b) the increased thermal hysteresis after the specimen is exposed to high stress cycling first and then subsequently to lower stresses.

between the applied stress and the transformation strain, and the last term is the elastic strain energy stored in the transforming domain due to the disturbance stress. The transformation criteria is written as follows,

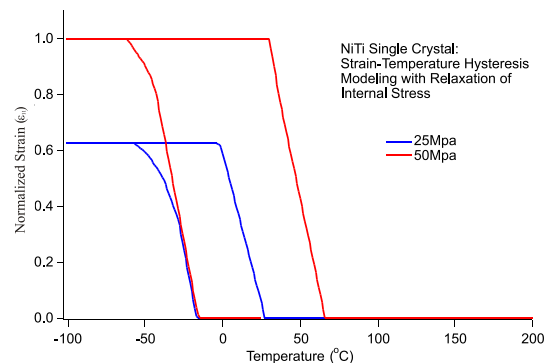
$$F^n = \frac{\partial \Psi}{\partial f^n} = B(T_o - T) + \Sigma_{ij} \varepsilon_{ij}^n - \sum_m H^{nm} f^m \geq F_c \quad (2)$$

where the critical value of driving force,  $F_c$ , is a material property. The evolution of the nth variant of martensite,  $f^n$ , can be determined from,

$$\frac{\partial \dot{F}^n}{\partial \Sigma_{ij}} \dot{\Sigma}_{ij} + \frac{\partial \dot{F}^n}{\partial f^n} \dot{f}^n + \frac{\partial \dot{F}^n}{\partial T} \dot{T} = -B\dot{T} + \dot{\Sigma}_{ij} \varepsilon_{ij}^n - \sum_m H^{nm} \dot{f}^m = 0 \quad (3)$$

The last term in Equation (1) is expressed using the interaction matrix  $H^{nm}$ . In the case of constant stress thermal cycling, the martensite volume fraction evolution is determined from Equation (3) as temperature is the imposed variable and  $\dot{\Sigma}_{ij} = 0$ . The response is strongly dependent on the non-chemical energy component which is the elastic stored energy within the martensite. The material constants used in the model can be found in Reference [8].

The elastic stored energy within a martensite is relieved due to introduction of dislocations loops effectively reducing the eigenstrain of the transforming inclusion. The nucleation of the interface dislocations is somewhat analogous to those formed due to misfitting precipitates in metallic materials except that crossslip (leading to prismatic loops) is not expected in NiTi materials. The exact nature of the dislocation segments due to the high shear stresses at the interfaces is not known at the moment. We provide a simple illustration of how the decrease in elastic stored energy in the transforming domains provides a widening of the thermal hysteresis. In the simulations shown in Figure 5, the strain axis is normalized by the maximum strain corresponding to 50 MPa. Simulations for the two stress levels are shown for 25 MPa and 50 MPa. In these simulations the magnitude of the  $H^{nm}$  matrix which is proportional to the transformation strain is decreased upon forward (austenite to martensite) transformation. Consequently, a higher thermal energy is needed to initiate the reverse transformation. The amount of reduction in the components of the  $H^{nm}$  matrix depend on the nature of the dislocations formed at the interface. At the moment, this is handled phenomenologically, and further studies are needed to elaborate the details of the relaxation process.



**Figure 5.** Simulation of the widening of the thermal hysteresis with increasing applied stress. The strain axis is normalized by the maximum transformation strain corresponding to 50MPa.

#### 4. DISCUSSION OF RESULTS

There has been early experimental research on the temperature hysteresis under constant stress. These studies are typically conducted on polycrystalline materials. The common finding in these studies has been that the thermal hysteresis decreases with increasing stress [9] under temperature cycling while others found an increase [10]. A constant thermal hysteresis, independent of stress, is also inherent in developing mechanics models for transformation which use DSC results as input parameters [4, 5, 8]. Similar trends have been observed and modeled for pseudoelasticity behavior under constant temperature where the stress hysteresis is assumed to be constant. There have not been systematic experimental studies studying the origin of hysteresis in shape memory alloys and the changes in hysteresis have not been well understood.

We note that the transformation temperatures increase linearly as the uniaxial stress is raised consistent with the Clausius-Clapeyron equation. This increase is noticeable but small compared to the large variations in thermal hysteresis with stress. The thermal hysteresis represents the temperature differential between the forward and reverse martensitic transformation. When the thermal hysteresis widens with applied stress such as in the 50.1%Ni case, this corresponds to a larger increase in the M->A temperature compared to the A->M temperature. On the other hand, in the 51.5%Ni case, the thermal hysteresis narrows with increasing stress (or increasing temperature) displaying a different behavior compared to the 50.1%Ni case. Such divergent trends have not been a focus of previous studies and require further interpretation and interrogation.

Microscopy revealed the presence of dislocations at the austenite/martensite interfaces. The nucleation of dislocation loops from the interfaces produces a modification of the stress fields within the martensite and the surrounding local field. An energy barrier has to be overcome in order to nucleate such a loop which depends on the transformation strain within the martensite, and the shape of the martensite. The externally applied stress facilitates the formation of dislocation loops. The emergence of these loops is to effectively reduce the eigenstrain (transformation strain) of the martensite hence lowering the magnitude of the internal energy in the transforming domains. The relaxation of the internal energy in the transforming domains produces a larger hysteresis upon reverse transformation from martensite to austenite. It is expected that, if a sufficient number of loops is generated in such a way to minimize the energy of the system, the relaxation associated with the dislocations considerably reduces the internal stresses.

The present experimental results under tensile stresses provide considerable insight into the role of detwinning of martensite plates on the transformation strains as well as on the thermal hysteresis. We

note that detwinning of the martensite for the [111] orientation is observed in the 50.1%Ni case while for the 51.5%Ni case the transformation strains fall short of the theoretical values. Detwinning occurs when an ensemble of variants collapse to a single variant with a resulting increase in elastic strain energy. This increase in elastic energy acts in opposition to the relaxation mechanisms operative due to dislocation motion. In Figure 3, the onset of detwinning for the 50.1% Ni case points to a change in the slope of the hysteresis versus stress curve confirming that detwinning competes with relaxation processes. This competition is believed to be responsible for the saturation of hysteresis levels in the low Ni NiTi alloy considered.

Contrary to the low Ni alloy, the high Ni (51.5%Ni) material resulted in a considerable decrease in the thermal hysteresis levels as the constant stress level was raised. These results were also consistent with the pseudoleasticity behavior at constant temperature which demonstrated a narrowing of the stress hysteresis with increasing temperature. The 51.5%Ni material has significant slip resistance [11] and electron microscopy results confirm much lower dislocation activity in the 51.5% case compared to the 50.1%Ni material. A lowering of the hysteresis in this material is a consequence of the build up of large internal stresses (hence increase in elastic strain energy) that facilitate the reverse transformation. We attribute the increase in elastic strain energy to the lack of relaxation in this case.

The experimental results are presented for the case of [111] single crystals with multiple interfaces of martensites. In the [111] orientation up to six martensite variants can be activated although fewer than six are observed experimentally. The mutual interaction of the martensite variants are accounted for in the thermodynamic modeling, and the results for polycrystals and single crystals with single martensite interfaces are expected to be qualitatively similar. We have conducted extensive set of experiments for the solutionized and aged [123], [012], [011] crystals with similar trends. The only orientation that display independent trends is the [001] case where there are no favorably oriented slip planes (in view of the B2 crystal structure). Therefore, unlike other orientations, in the [001] case the hysteresis does not grow with increasing stress in the case of 50.1%Ni crystals.

## 5. CONCLUSIONS

The work supports the following conclusions:

- (1) The thermal hysteresis width grows with increasing stress in low Ni (50.1%Ni) NiTi alloys, while it narrows with increasing stress in the high Ni (51.5%Ni) case. The results meet the Differential Scanning Calorimetry measurements in the limit of zero stress.
- (2) The relaxation of elastic stored energy due to dislocation generation is primarily responsible for the growth of thermal hysteresis with increasing stress. Although the exact geometry of the dislocations emanating from the martensite/austenite interfaces is not yet established, the net effect is the reduction of internal stress and transformation strain.
- (3) The thermal hysteresis possesses a memory of previous high stress thermal cycles, due to the imposed dislocation arrangements. On the other hand, under constant stress thermal cycling, the single crystals did not exhibit variation from cycle to cycle.
- (4) A thermodynamic description which allows modification of the internal energies due to slip processes has been forwarded. It is shown that this type of modeling can be modified to capture the changing thermal hysteresis with increasing stress.

## Acknowledgements

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