Session 3164

NiTi – Magic or Phase Transformations?

Katherine C. Chen
Materials Engineering Department
California Polytechnic State University, San Luis Obispo, CA 93407

Abstract

NiTi alloys possess exciting properties and are staples in materials demonstrations. The shape memory effect and superelasticity property of NiTi fascinate people, but actually require significant materials knowledge to fully understand the phenomena. A laboratory dealing with phase transformations was thus developed to capitalize on the allure of NiTi for a junior/senior level "Thermodynamics and Kinetics of Materials" course.

Students examine and characterize the ***shape memory*** and ***superelastic*** properties of NiTi wire, and then realize the difference is in the transformation temperature (i.e., A_f - the austenitic finish temperature). They then use the phase diagram and TTT diagram to develop the appropriate annealing treatments to change a sample from superelastic into shape memory behavior. Concepts of precipitation, kinetics, nucleation and growth are incorporated into the lab. Students can then also "train" the NiTi wires into desired shapes. Several different conceptual levels of phase transformations may be investigated according to learning objectives for different audiences.

Introduction

The shape memory effect and superelastic properties of NiTi alloys serve as fun demonstrations or "party tricks" to amuse the young and old. Often times people will claim that the materials are "magic," but in reality, these materials demonstrate fascinating processing-structure-properties relationships for materials science and engineering students!

A laboratory has been developed to thoroughly understand the mechanisms and the origins for the properties. Students examine and characterize the *shape memory* and *superelastic* properties of NiTi wire, and then realize the difference is in the transformation temperature (i.e., A_f - the austenitic finish temperature). They then use the phase diagram and TTT diagram to develop appropriate annealing treatments to change "as-received" samples from superelastic into shape memory conditions. Concepts of precipitation, nucleation and growth, and kinetics are incorporated into the lab. The lab is somewhat open-ended and asks the students to formulate explanations for the observed trends.

The goal of the lab is to demonstrate and investigate the phase transformations of NiTi due to stress and/or temperature. The learning objectives are as follows:

- identify the different phases and crystal structures of NiTi
- identify the region (i.e., phase field) on the phase diagram (T, composition) where NiTi is thermodynamically stable
- demonstrate and differentiate between the *shape memory effect* and *superelasticity*
- explain why annealing can change the A_f (using the phase diagram and TTT diagram)
- design and perform the necessary heat treatment to achieve a specific transformation temperature or transformation stress (e.g., change from superelastic to shape memory)
- identify the start and end of the phase transformations (i.e., A_s, A_f, M_s, M_f) on a DSC scan
- discuss the effect of test temperature (i.e., below and above A_f) on the mechanical behavior of NiTi
- determine the stress needed to start the martensitic transformation (i.e., superelasticity) by tensile tests
- relate the plateau stress and A_f to the heat treatment (i.e., processing-structure-properties relationships) of the NiTi samples
- propose applications for the shape memory effect and for the superelastic effect of NiTi

Background or Lecture Topics

<u>NiTi Phase Transformations</u>

The unique behavior of NiTi is based on a *thermoelastic* (i.e., thermal and mechanical) *phase* (or crystal structure) *transformation*. The high temperature (or *parent*) phase is known as "austenite" and has the ordered intermetallic crystal structure, B2 or CsCl ($Pm\bar{3}m$). At particular temperatures or strains, the austenite transforms into "martensite," which has a monoclinic crystal structure ($P2_1/m$).

If the parent phase is cooled below M_f (the martensite finish temperature), the austenite completely transforms to martensite, yet the bulk macroscopic shape is left intact! However, on the atomic scale, several different martensite variants have been created and are twinned to maintain the original bulk shape (Figure 1). There are a total of 24 possible crystallographically-

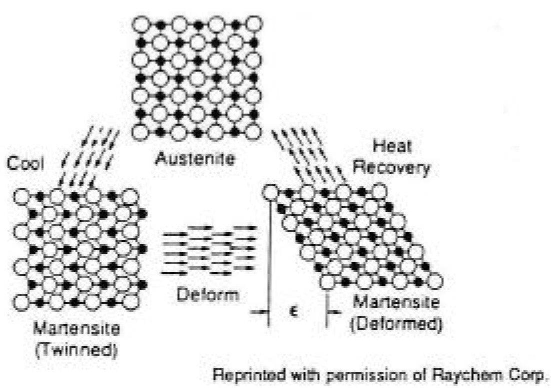


Figure 1. Phase changes associated with the shape memory effect[1].

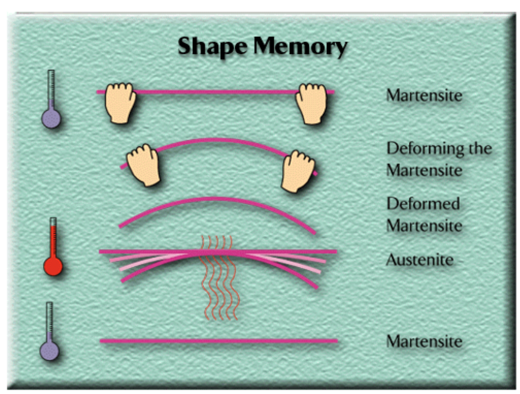


Figure 2. Demonstration of the shape memory effect[2].

equivalent habit planes of martensite. Once in the martensite form, the material is easily deformable through twinning. Particular variants grow at the expense of others to produce *plastic* deformation of shape change.

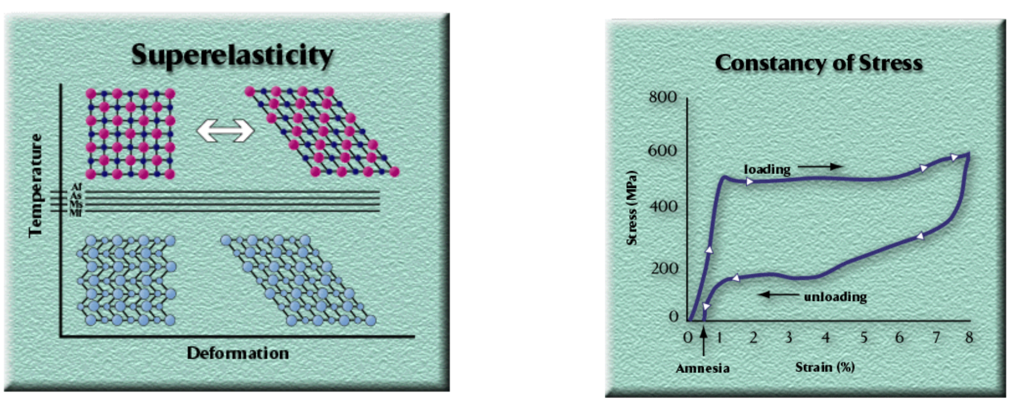
While most metals deform by slip or dislocation movement, NiTi responds to stress by simply changing the orientation of its crystal structure through the movement of twin boundaries. A NiTi specimen will deform until it consists only of the correspondence variant (crystallographic orientation), which produces maximum strain. However, deformation beyond this will result in classical plastic deformation by slip, which is irrecoverable and a "permanent set" will result.

The ***shape memory effect*** (Figure 2) occurs when shape change occurs through martensitic twin reorientation and then the material is heated above A_f (the austenite finish temperature) to induce the phase transformation. Since there is only <u>one</u> possible parent phase (austenite) orientation, all martensitic configurations revert to that single defined structure and shape upon heating.

Superelasticity refers to the ability of NiTi to return to its original shape upon unloading after substantial deformation, similar to stretching a rubber band (Figure 3). This phenomenon is based on *stress-induced* martensite formation. The application of an applied stress causes martensite to form at temperatures higher than M_s (martensite start temperature). With stress-induced martensite, only one variant is formed that is parallel to the direction of the applied stress. When the stress is released, the martensite transforms back into austenite, and the specimen returns back to its original shape. Thus, <u>stress</u> rather than temperature causes the phase transformation.

<u>Heat Treatments of NiTi</u>

With knowledge of *processing-structure-properties* relationships, materials engineers can tailor materials to have the desired properties and performances. In order to harness the unique properties of NiTi, control of the transformation temperatures and/or stress is essential. The A_f temperature is determined primarily on the specific Ni-Ti alloy composition. <u>In general, increasing the Ti content of the NiTi leads to an increase in the A_f.</u> Examination of the equilibrium phase diagram[3] of the Ni-Ti system (Figure 4) reveals that NiTi is stable only at temperatures above 630°C!



(a) (b)

Figure 3. a) Superelasticity involves the stress-induced phase transformation of austenite to martensite. b) The plateau stress is associated with the martensitic transformation[2].

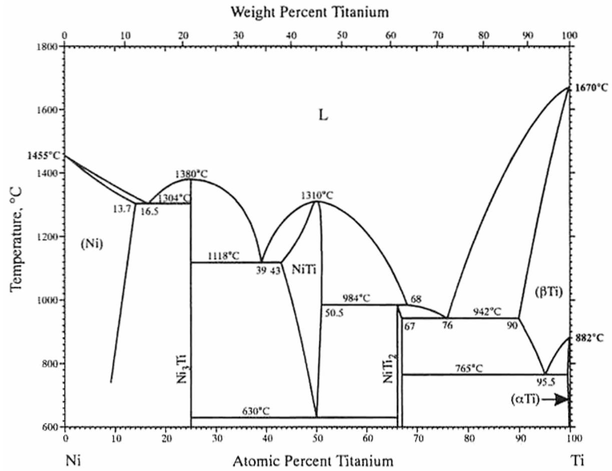


Figure 4. The Ni-Ti phase diagram[3].

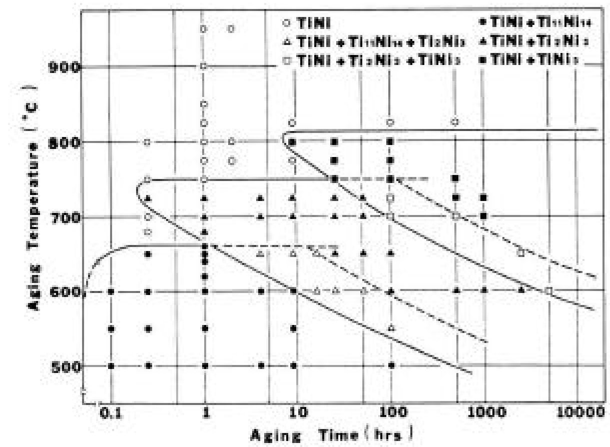


Figure 5. TTT diagram describing aging behavior for Ti-52Ni[4].

The phase diagram and TTT diagram (Figure 5) assist in determining the phase transformations with isothermal holds outside the NiTi single-phase field. The TTT diagram suggests that *metastable* precipitation will first occur[4], and in turn, the A_f of the NiTi can change. Thus, manipulation of the transformation temperatures is possible!

Laboratory Procedures

Heat Treatments

As a class, students construct a heat treatment test matrix (grid of test times and temperatures) that will produce a range of A_f's, and thus, different mechanical properties. Each group is responsible for one heat treatment *temperature*. Every group then conducts heat treatments at the same annealing *times*. The goal of this experiment is to produce a range of A_f's. In the end, a TTT-like diagram that gives contours of A_f temperatures is produced by the class.

After heat treating, the students deform the NiTi wires and determine which phase (i.e., martensite or austenite) is present at room temperature. The temperature in which the deformed wire "remembers" its shape is the A_f. Hot plates and beakers of water (or other mediums) are used to get "ballpark" numbers for the A_f's.

Differential Scanning Calorimetry (DSC)

Each group cuts off a small piece from the end of each heat-treated wire, and performs DSC on each sample. The "ballpark" temperatures are used to assist the selection of temperature ranges to use for the DSC. Students determine the A_s, A_f, M_s, M_f temperatures (Figure 6), and the heat of transformation (ΔH) for each sample. The students are then asked to discuss and explain the trends they find.

Tensile Test

Each group also pulls an as-received wire and their heat-treated wires with a tensile tester to generate a stress-strain plot. The plateau stress indicates the stress required for the martensitic

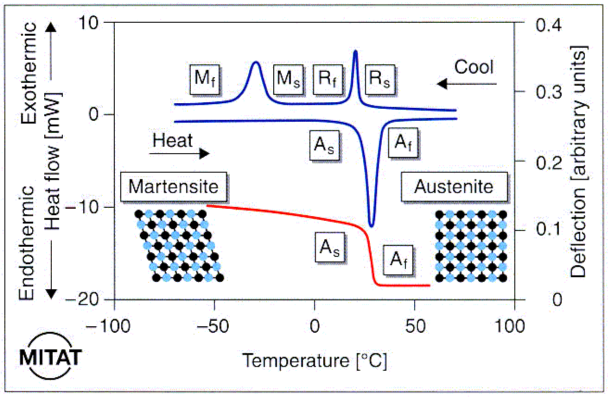


Figure 6. Differential scanning calorimetry and free recovery of the same processed wire. Note that upon cooling the wire transforms to R-phase prior to the martensitic transformation. Upon heating, both techniques provide similar A_s and A_f temperatures as the (monoclinic) martensite transforms to the (cubic) austenite.[5]

transformation or superelasticity (Figure 7). The trends of the transformation stress with the annealing temperatures and times can be related the trends to the DSC data.

All groups in the class share their DSC and tensile test data in order to observe the trends in properties due to the different processing treatments. A TTT-like diagram can then be assembled that plots contours of the A_f temperatures on a plot of temperature versus time. In addition, the students are asked to discuss the how and why's of the following:

- heat treatment effects the loading or stress plateau
- C-curves on contour plots of the A_f temperatures
- correlation of the trends of the DSC and tensile test results

Results

The plot of A_f temperatures should resemble C-curves, as in Figure 8. Essentially, Ni-rich precipitates are formed during the annealing treatments (outside of the single-phase region), which results in a more Ti-rich NiTi matrix. The small change in NiTi composition results in the change in A_f, and can take the material from *superelastic* (A_f below room temperature) to *shape memory* (A_f above room temperature). Since the whole process of changing the A_f's is governed by the precipitation of Ni-rich phases, the kinetics follow nucleation and growth behavior.

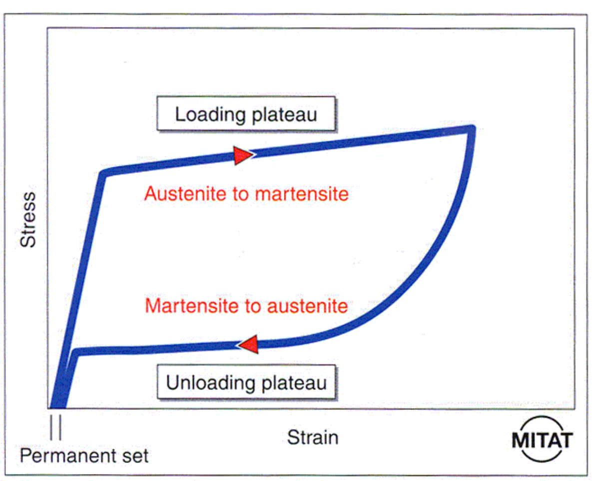


Figure 7. Schematic stress–strain curve of superelastic Nitinol. There is a transformation from austenite to martensite that begins at the apparent yield stress. The plateau stress remains nearly constant with increasing strain as the amount of martensite increases. Upon unloading, the martensite reverts to austenite along the unloading plateau. The 'permanent set' measures any residual strain.[5]

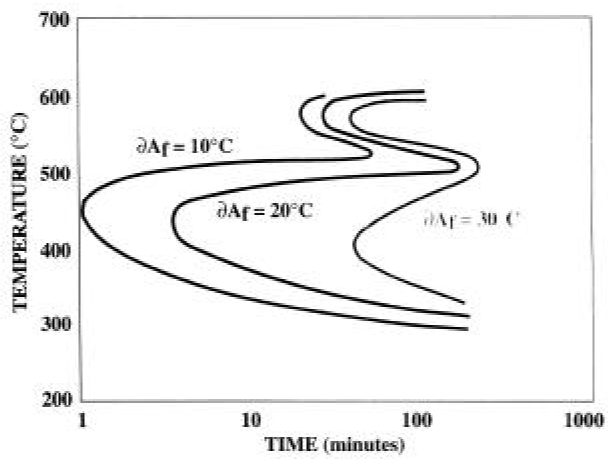


Figure 8. Contour curves of changes in the Af temperature of NiTi upon annealing at specific temperatures and times[6].

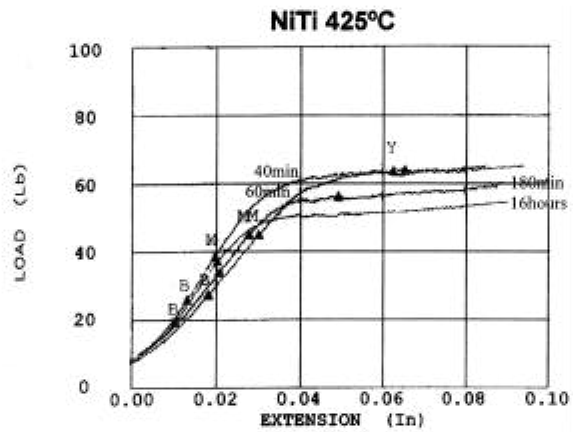


Figure 9. Tensile test results for NiTi heat-treated at 425°C for four different times. Longer anneal times produce lower plateau stresses for the martensitic transformation due to higher A_f temperatures (that are closer to room temperature).

In addition, the plateau stress of the austenitic samples should increase with samples of decreasing A_f temperatures. A sample with a low A_f, relative to room temperature, can be considered to be far from the transition point, and thus a larger stress (or change in temperature) is needed to start the transformation. A sample plot of load vs. extension from the actual lab is shown in Figure 9. The plateau stress decreases as the heat treatment time increases, and the A_f gets closer to room temperature. If the samples are martensite at room temperature, a very low "plateau stress" will appear, since deformation by twinning occurs (as opposed to transforming).

This particular lab experience has been rated favorably by the students in the past couple years of its existence. The design of the lab actually originated from students interested in NiTi, and has grown in complexity. The Ni-Ti equilibrium phase diagram, TTT diagram, and knowledge about kinetic processes (e.g., diffusion, precipitation, phase transformations) are all invoked for the analysis. Students enjoy the ability to plan parts of the experiment and witnessing the connection between theory and experiment.

Bibliography

1. http://www.sma-inc.com/
2. http://www.nitinol.com/
3. Phase Diagrams for Binary Alloys, ASM International, 2000.
4. M. Nishida, C.M. Wayman, and T. Honma, *Met Trans* 17A, 1505, 1986.
5. A.R. Pelton, J. DiCello and S. Miyazaki, *Min Invas Ther & Allied Technol* 2000: 9(1) 107.
6. J. Sheriff, NDC, private communications.

Biography

KATHERINE C. CHEN is an Associate Professor in the Materials Engineering Department at Cal Poly State University, San Luis Obispo, CA. She received her bachelor degrees (in Chemistry and Materials Science & Engineering) from Michigan State University, and Ph.D. from the Massachusetts Institute of Technology. At Cal Poly, she teaches the undergraduates Structures of Materials, Kinetics of Materials, and various other courses.