NiTi – Magic or Phase Transformations?

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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**

**NiTi Phase Transformations**

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-
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 one 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, stress rather than temperature causes the phase transformation.

Heat Treatments of NiTi
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. In general, increasing the Ti content of the NiTi leads to an increase in the $A_f$. Examination of the equilibrium phase diagram of the Ni-Ti system (Figure 4) reveals that NiTi is stable only at temperatures above 630°C!

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.
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, 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 ($\Delta H$) 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
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.
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

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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.