NITINOL, A NICKEL-TITANIUM SHAPE MEMORY ALLOY (SMA)

DEPARTMENT OF CHEMISTRY
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Introduction

In this experiment, you will investigate a “smart” nickel-titanium alloy called nitinol (pronounced “night in all”). The name of this material derives from its composition (nickel and titanium) and the place of its discovery (the Naval Ordnance Laboratory). Nitinol, which is composed of equiatomic (or near equiatomic) amounts of Ni and Ti, is an example of a shape memory alloy (SMA). When plastically deformed under certain conditions, this material can restore its original shape if heated above a certain threshold temperature called the transformation temperature. This “shape memory” effect is the result of a temperature-dependent, solid-state phase transformation between the low-temperature martensite and high-temperature austenite crystalline phases. This temperature-induced (or stress-induced) phase change involves a subtle shift or rearrangement of the atoms in the solid.

The unit cells of the austenitic and martensitic phases of nitinol are shown below in Figure 1.

![Unit Cell of the Austenitic Phase of Nitinol](image1.png) ![Unit Cell of the Martensitic Phase of Nitinol](image2.png)

**Figure 1.** Unit cell depictions of the austenite and martensite phases of nitinol. (From *Chemistry for Engineers*, M.J. Shultz.)

As depicted, the unit cell of the martensitic phase is distorted with respect to that of the austenite phase. At low temperatures, nitinol adopts the soft, easily-deformed martensite phase. Heating the solid above the transformation temperature causes the structure to convert to the more rigid austenite phase. The schematic in **Figure 2** shows the mechanics of this conversion.
Figure 2. This schematic shows the temperature-dependent solid-state phase transition that occurs between the martensitic and austenitic forms of nitinol. The mechanics of the shape memory effect are also depicted. The structures labeled $A$, $B$, and $C$ represent the martensite, deformed martensite, and austenite phases, respectively.

In Figure 2, the grid patterns represent the two-dimensional lattice structures of the different solid-state phases. As depicted, heating the martensitic phase (structure $A$) leads to a rearrangement of the atoms and the formation of the austenitic phase (structure $C$). Subsequent cooling leads to the reverse transition. The “origin” of the shape memory effect is also portrayed in this diagram. High temperature ($> 500 \, ^\circ\text{C}$) treatment of nitinol can be used to “train” the alloy so that it adopts a specific austenitic shape when above the transformation temperature. The “trained” shape will persist upon cooling and relaxation to the martensitic phase. Nitinol is flexible and easily deformed in the low-temperature martensitic phase (as depicted in the $A \rightarrow B$ transition). However, as long as this deformation is not too severe, subsequent heating above the transformation temperature will cause the “deformed” martensitic material (structure $B$) to revert back to the highly-ordered austenitic structure (structure $C$). In other words, the material will recover its “trained” shape.

In this five-part experiment you will (1) explore nitinol’s solid-state phase transformation and shape memory behavior, (2) identify a series of unknown wires, (3) measure the transformation temperature for a nitinol sample, (4) “retrain” a nitinol wire to a new austenite shape, and (5) examine the acoustic properties of martensitic and austenitic nitinol through an online investigation.
Pre-lab

Safety: Goggles must be worn at all times. Take care when working with hot plates, hot water, and hot glassware. Avoid touching the top or sides of the hot plate with your body or with the cord on the Vernier temperature probe. When immersing the nitinol wire in hot water or retraining the wire in a flame, make sure that you always hold on to the wire in such a way that you avoid burning your fingers and hands. The use of forceps, pliers, or tongs is recommended for this purpose. When retraining your nitinol sample, make sure all flammable objects are removed from the immediate vicinity of the candle flame. Always use caution with fire, and never leave the burning candle unattended. When using resistive heating to activate the phase transformation, do not keep the 9 V battery connected to the nitinol wire for more than ~10 sec. Disconnect the battery immediately if it becomes hot. Care should always be taken when transporting materials across the lab.

Pre-lab Assignment: Please write out the following in your lab notebook. This assignment must be completed before the beginning of lab. You will not be allowed to start the experiment until this assignment has been completed and accepted by your TA.

1) Briefly describe the objectives of this experiment.

2) Write out the experimental procedure in your lab notebook according to the “Guidelines for Keeping a Laboratory Notebook” handout.

In addition to these pre-lab requirements, a short quiz will be given at the beginning of lab based on the material in this lab write-up, read through the write-up in its entirety. A useful Journal of Chemical Education article titled Nickel-Titanium Memory Metal: A “Smart” Material Exhibiting a Solid-State Phase Change and Superelasticity by Gisser et al. is posted on the lecture course Blackboard site.

Procedure

Part 1 – Tinkering with a “Smart” Toy

Follow the instructions below for a hands-on look at the shape memory alloy nitinol.

1. Fill a 250 mL beaker with ~100-200 mL of water. Place the beaker on one of the hot plates in the laboratory. (Note: The circuitry in the lab limits the number of hot plates that can be used at a given time. Hence, groups will have to share hot plates.) Turn the hot plate on and monitor the temperature of the water using a Vernier temperature probe and the Logger Pro software. Continue on to the next step while the water heats to ~60 °C.
2. Obtain a “Live Wire” from your TA. This is a commercially-available nitinol wire produced by the TiNi Alloy Company. This SMA wire, which has a bead attached to each end, has been “trained” so that it adopts a curved shape. Please handle this wire with care as it will be used throughout the entire week.

3. Take the “smiling” wire out of the packaging. Examine the flexibility of the wire by gently straightening and bending it. (CAUTION: When bending this wire, you must avoid sharp bends or kinks as this can overstrain the wire and prevent shape recovery.) Record your observations, including wire color and flexibility, in your notebook.

4. Straighten the wire again. Use a pair of pliers or forceps to grasp the bead on one end of the now-straightened wire. Dip the wire into the water that has been heated to ~60 °C and observe any changes that occur. (CAUTION: When doing this, make sure that you hold on to the wire in such a way that you avoid burning your fingers or hands. Also, avoid touching the top or sides of the hot plate with your body.) Remove the wire from the hot water, and record your observations in your notebook. Make sure that you describe any transformation that was observed. Comment on the force and rate of the change. What was the shape of the wire when you removed it from the hot water? What was the shape of the wire after you gave it time to cool off?

5. After the wire has cooled (~1-2 min), coil it in a helical pattern around one of your fingers. Remove the wire from around your finger, and then dip it in the hot water in the same manner as you did in Step 4. Record your observations.

6. Once the wire has cooled, dry it off with a paper towel.

7. As you saw in the nitinol spring demonstration, resistive heating can also be used to demonstrate the shape memory effect in nitinol. Obtain a 9 V battery and a battery snap connector outfitted with alligator clip leads. Deform your nitinol wire by straightening or bending it. Connect the battery snap to the battery terminals. Attach the alligator clips to opposite ends of the nitinol wire. (Avoid touching the nitinol wire when you do this.) Observe the change in the shape of the nitinol wire. (CAUTION: Do not keep the battery connected to the wire for more than ~10 sec. Disconnect the battery immediately if it becomes hot.) As the current passes through the nitinol wire, the wire will heat up, which will activate the solid phase transformation and restore the austenite shape. Take note of the flexibility of the wire once it has transformed to the high-temperature phase. Record your observations in your notebook. Disconnect the alligator clips from the wire. Remove the snap connector from the battery terminals. Allow the wire to cool off.

8. Make sure the wire is in its “trained” shape. Return the wire to its original packaging, and give the wire back to your TA. Return the 9 V battery and the snap connector to their proper storage location in the laboratory.
Discussion and Analysis: Your observations and associated explanations should be discussed in your laboratory report. Make sure that you respond to all of the questions posed in the procedures. You should also comment on the flexibility of the martensitic and austenitic phases. Give an atomic-level explanation for the observed differences in flexibility. Suggest other methods of heating (besides immersion in hot water and resistive heating) that one might use to induce the solid-state phase transformation. Explain why this particular shape memory effect is called a “one way memory effect.”

Part 2 – Identifying a Set of Unknown Wires

In the second part of this experiment, you will be given five different wires. Each of these wires is composed of a different material, namely aluminum, copper, nickel, nitinol, or titanium. The purpose of this exercise is to determine the identity of each wire. Correct identification of the nitinol wire is important as you will need this wire later in this experiment.

1. Each group will be assigned a box of unknown wires. Open your box and verify that there are 5 wires in your box, each enclosed in a numbered bag. Do not remove the wires from the bags until instructed to do so. Construct a table in your lab notebook similar to the one given below.

<table>
<thead>
<tr>
<th>Bag #</th>
<th>Wire Color</th>
<th>Wire Length</th>
<th>Wire Diameter</th>
<th>Wire Mass</th>
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</thead>
<tbody>
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</tbody>
</table>

2. Remove the wire from one of the bags. Record the bag number and wire color in Table 1. Measure the length, diameter, and mass of the wire using a ruler, a micrometer (or caliper), and an analytical balance, respectively. Record these data and their associated units in your notebook. All data should be recorded with the appropriate significant figures. Place the wire back in its original, numbered bag. Seal the bag, and return it to the box.

3. Repeat Step 2 for the remaining wires making sure that only one wire is removed from its bag at any given time. This will ensure that the wires are not mixed up and subject to misidentification. Failure to follow these instructions may result in significant point deductions. False identification of the nitinol wire is particularly problematic as this wire is needed later in the lab. Each wire should be returned to its original, numbered bag and placed in the box once you have finished the necessary measurements. After data collection is complete, seal the box.
4. Calculate the density (in g/cm³) of each wire using the data collected in Table 1. Assume the wire has a cylindrical shape such that \( V_{wire} = \pi r^2 L \), where \( V_{wire} \) is the volume of the wire, \( r \) is the radius of the wire, and \( L \) is the length of the wire. All calculations should be shown in your notebook and organized in an easy-to-follow, logical way. A sample calculation should also be included in your laboratory report.

5. The densities of aluminum, copper, nickel, and titanium are 2.6989 g/cm³, 8.96 g/cm³, 8.902 g/cm³, and 4.54 g/cm³, respectively. The density of nitinol is 6.45 g/cm³. Compare your calculated densities with these literature values to help you identify each wire. Wire color may also prove useful during this identification process. Pictures of each metal can be found on Theodore Gray’s online periodic table (http://periodictable.com/) or on WebElements (http://www.webelements.com/). Reasonable justification and explanation must be provided for each prediction in order to receive full credit.

6. For each material, calculate the percent error between your measured density and the “accepted” value (i.e., the literature value). Percent error is given by:

\[
\% \text{ Error} = \left( \frac{\text{measured value} - \text{accepted value}}{\text{accepted value}} \right) \times 100%
\]

7. Verify with your TA that you have correctly identified the nitinol wire. Take this wire out of the box and remove it from the numbered, plastic bag. Keep this wire as it will be needed later in the lab. All of the remaining wires should remain in the box. The empty bag that once contained the nitinol wire should be returned to the plastic box. Seal the box and return it to the proper storage location in the laboratory. Your TA will check these boxes at the end of the lab period. Failure to follow instructions will result in point deductions.

**Discussion and Analysis:** Your observations and associated explanations should be discussed in your laboratory report. As instructed, a sample density calculation must be included in your report. Discuss possible sources of error that may have affected your calculated densities. Rank your list of potential sources of error in terms of perceived importance (i.e., give some indication of which source or sources most likely contributed to any observed discrepancies). You are not expected to provide a formal error analysis, but you should at least think about factors that might have influenced the accuracy of your measurements and/or calculations.

**Part 3 – Estimating the Transformation Temperature for a Nitinol Wire**

In this part of the exercise, you will determine the transformation temperature of the nitinol wire identified in Part 2. Specifically, you will deform the room-temperature martensitic wire, immerse it in water, heat the water on a hot plate, and monitor the shape recovery process as the wire heats up. The temperature at which the wire becomes rigid
and has returned to its original, linear configuration (meaning it has transformed from the martensite phase to the austenite phase) is the transformation temperature.

In this experiment, both the austenite start temperature, \( A_s \) (the temperature at which the wire begins to restore its austenitic shape), and the austenite finish temperature, \( A_f \) (the temperature at which the wire finishes the martensite-to-austenite transition), will be measured. Class data will be compiled in order to calculate average values for \( A_s \) and \( A_f \).

1. Bend your nitinol wire in the center as shown at right.

2. Obtain a 100 mL beaker and fill it with water. Place the beaker on a hot plate. Monitor the temperature of the water using a Vernier temperature probe and the Logger Pro software. Attach a double buret clamp to a ring stand, and use the clamp to hold the temperature probe in the water (see the photo on the right). Make sure that the probe does not touch the sides or bottom of the beaker.

3. Attach a small, three-prong extension clamp to a second ring stand. Secure one end of the nitinol wire in this clamp. Position the ring stand and adjust the height of the clamp so that the bend in the nitinol wire is fully immersed in the water (as shown on the left). You may need to add more water to the beaker to ensure that the deformed section of the wire is completely immersed. Make sure that the temperature probe and the nitinol wire are close to one another but do not touch. The wire should not touch the sides or the bottom of the beaker. Confirm that the wire is positioned in such a way that it is easy to monitor the change in shape as it heats up. Also make certain that the wire will not be impeded by the beaker or the probe as it recovers its linear shape. Reposition the wire as deemed necessary.
4. Turn on your hot plate and slowly warm the water. Closely monitor your wire as it heats up. Record the temperature at which the wire begins to straighten. This is the austenite start temperature ($A_s$). Record the temperature at which the wire has fully restored its original, linear configuration. This temperature is the austenite finish temperature ($A_f$).

5. Remove the nitinol wire from the clamp assembly and keep it for Part 4. Make sure you return the ring stands to their proper storage location in the laboratory. Turn off the hot plate.

6. List your measured values of $A_s$ and $A_f$ on the chalkboard. Construct a table in your notebook similar to the one shown below. As each group writes their measured values of $A_s$ and $A_f$ on the board, add these data to Table 2. Make sure that you get data from every group before you leave lab for the day.

<table>
<thead>
<tr>
<th>Group</th>
<th>$A_s$ (°C)</th>
<th>$A_f$ (°C)</th>
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<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
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<td>3</td>
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<td>4</td>
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<tr>
<td>5</td>
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</tbody>
</table>

Discussion and Analysis: Your observations and associated explanations should be discussed in your laboratory report. Calculate average values of the austenitic start ($A_s$) and finish ($A_f$) temperatures using the class data. Compare your measurements with the class average. Discuss possible sources of error that may have affected your measurements.

Part 4 – “Retraining” the Nitinol Wire to a New Shape

Now let’s “train” your nitinol wire to remember a new shape. This will be accomplished by holding the wire in a desired shape and then heating it above 500 °C in a flame. This heat treatment should provide sufficient thermal energy to “fix” a new austenite shape.

1. Use a utility lighter or match to light a candle. (CAUTION: Always use caution with fire, and never leave a burning candle unattended. Make sure all flammable objects are removed from the immediate vicinity of the flame.)

2. Grasp each end of your room-temperature nitinol wire with a pair of needle-nose pliers. Bend the wire into a desired shape. (Consider just bending the wire in a “U” shape to start off.) Hold the wire with the pliers so that the wire maintains this configuration.

3. Hold firmly onto the wire as you bring it close to the flame. (CAUTION: Exercise caution to avoid burning yourself or causing an accidental fire.) As you initially heat
the wire, it will try to straighten and return to its original shape. Heat the wire until you feel a distinct “give” in the wire as the tension releases. When this occurs, remove the wire from the vicinity of the flame. Avoid overheating the wire, as this can damage it. Continue holding the wire in the newly trained shape as it cools to room temperature (~1-2 min). Record your observations in your notebook.

4. Once your wire has cooled, check to see if you have successfully retrained your nitinol wire by deforming it then heating it above the transformation temperature in hot water. Record your observations in your notebook.

5. Repeat Steps 2 and 3 and try to retrain your wire back its original, linear form. Record the success of this effort.

6. Blow out your candle. Return the candle, the utility lighter, and the pliers to their proper storage location in the laboratory.

Discussion and Analysis: Your observations and associated explanations should be discussed in your laboratory report. In your report, you should discuss why heating your memory metal sample over 500 °C should allow it to take on a new “remembered” shape. If your shape-training efforts were unsuccessful, discuss possible reasons for this.

Part 5 – Can You Hear Me Now? - Investigating the Acoustic Properties of Nitinol

William J. Buehler’s 1959 discovery of the temperature-dependent acoustic properties of solid nitinol was one of the first indications that this material undergoes a reversible solid-state phase transformation at relatively low temperatures. The acoustic properties of martensitic and austenitic nitinol are discussed in the JCE article by Gisser et al. You can learn more about these properties by visiting: http://chemistry.beloit.edu/edetc/cineplex/sound/index.html. This “NiTi Phase” website, which was developed by the Interdisciplinary Education Group at the University of Wisconsin-Madison Materials Research Science and Engineering Center (UW MRSEC), is part of the UW MRSEC “Exploring the Nanoworld” project. Go to this website. This particular page is part of their demonstration Cineplex devoted to nitinol. Watch the “Austenite phase NiTi” cooling and heating videos and the “Martensite phase NiTi” cooling and heating videos by clicking on the associated images (sound is required). Answer the following questions after you have finished watching these four video clips.

1) How can the acoustic properties of nitinol be used to determine whether a rod of this material is in the martensite or austenite phase?

2) Which phase produces a dull “thud” when dropped? Which phase produces a “ringing” sound when dropped?

3) Why do the different phases of nitinol have different acoustic signatures?

Click on the image labeled “Can you solve a NiTi mystery?” In this interactive video module, you will solve a mystery using your knowledge of the different acoustic signatures of martensitic and austenitic nitinol. Web camera footage and witness
accounts will be used in conjunction with independent laboratory measurements to determine who committed the crime. Complete this online memory metal mystery and answer the following questions.

4) What was the “crime” that was committed in the video module?

5) What piece of evidence was dropped by the obviously very clumsy criminal?

6) When the object was dropped, what sound did it make when it was (a) cold, (b), hot, and (c) at room temperature?

7) Who committed the crime?

8) At the end of this criminal investigation, what reward were you given for your crime sleuthing efforts?

Discussion and Analysis: Your answers to these questions should be included in your laboratory report.

Report

Your lab report should be a formal, individual report that addresses all the questions posed in this write-up, including those listed in the Discussion and Analysis sections. This document should be prepared according to the instructions given in the “Guidelines for Laboratory Reports” handout.