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Experiment 10

A Shape Memory Alloy, NiTi

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Notes for Instructors

Purpose

To explore the physical properties of NiTi (nitinol) and to determine the transition-temperature range of the NiTi solid-state phase change.

Method

The temperature (and phase) of the sample is adjusted by placing a sample in a water bath. NiTi in the low-temperature phase makes a soft "thud" sound when dropped on a surface; in the high-temperature phase it makes a louder "ring" sound. *See* Figure 1. This feature allows the temperature range over which a NiTi sample changes its phase to be determined acoustically. *See* Chapter 9.

Materials

NiTi wire (*see* Supplier Information)

Low-temperature phase NiTi rods (*see* Supplier Information)

High-temperature phase NiTi rods (*see* Supplier Information)

Beakers

2725-X/93/0423$06.00/1

Hot plates

Tongs

Candles and matches

String (thin string or thread)

Foam cups

Liquid nitrogen

Results

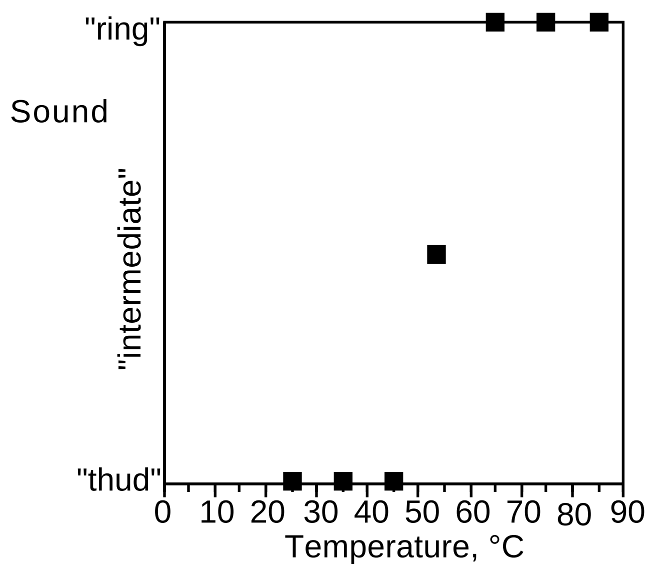

Figure 1. Typical results for the transition temperature study. The phase transition usually occurs over about a 10°C interval.

A Shape Memory Alloy, NiTi

Purpose

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Introduction

Nitinol is an acronym for an alloy of nickel and titanium that was discovered in the early 1960s at the Naval Ordnance Laboratory (Nickel Titanium Naval Ordnance Laboratory). Its relative inertness to many chemical reagents led scientists to study nitinol's value as a rust-resistant alloy for ships. However, it was also discovered that the alloy could be mechanically deformed, and by applying heat, restored to its original shape. Compounds that “remember” their original shape are called shape memory alloys. NiTi is probably the most well-known of the shape memory alloys; other such alloys include gold–cadmium, copper–aluminum, and copper–aluminum–nickel.

The shape to which a piece of NiTi will return (or “remember”) is set into the alloy by annealing at temperatures of 500–550 °C. At these temperatures, the nickel and titanium atoms crystallize in the CsCl structure, as shown in Figure 1. Each titanium atom is surrounded by eight nickel atoms, and each nickel atom is surrounded by eight titanium atoms. This high-temperature crystalline phase is called austenite. When the sample is cooled to lower temperatures, the nickel and titanium atoms shift slightly to form a less symmetric crystalline structure called martensite. The transition between these two crystal structures is an example of a solid–solid phase transition. If the alloy is bent while in the martensite phase, the original shape of the metal can be recovered by heating the sample back to the austenite phase.

The temperature range over which the alloy passes from the martensite phase to the austenite phase (or vice versa) will vary, depending upon the composition of the alloy. Although the ratio between nickel and titanium atoms in NiTi is close to 1:1, even a slight deviation from this value can cause a noticeable change in the temperature of the transition (Figure 2).

NOTE: This experiment was written by Kathleen R. C. Gisser, Margret J. Geselbracht, Ann Cappellari, Lynn Hunsberger and Arthur B. Ellis, Department of Chemistry, University of Wisconsin—Madison, Madison, WI 53706; John Perepezko, Department of Materials Science and Engineering, University of Wisconsin—Madison, Madison, WI 53706; and George C. Lisensky, Department of Chemistry, Beloit College, Beloit, WI 53511.

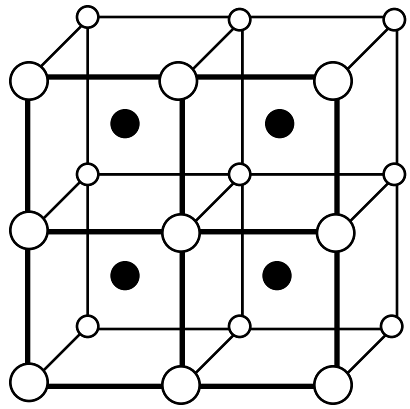

Figure 1. Four unit cells of the crystalline structure of the high-temperature phase of nitinol. Filled circles represent nickel atoms, and open circles represent titanium atoms (or vice versa).

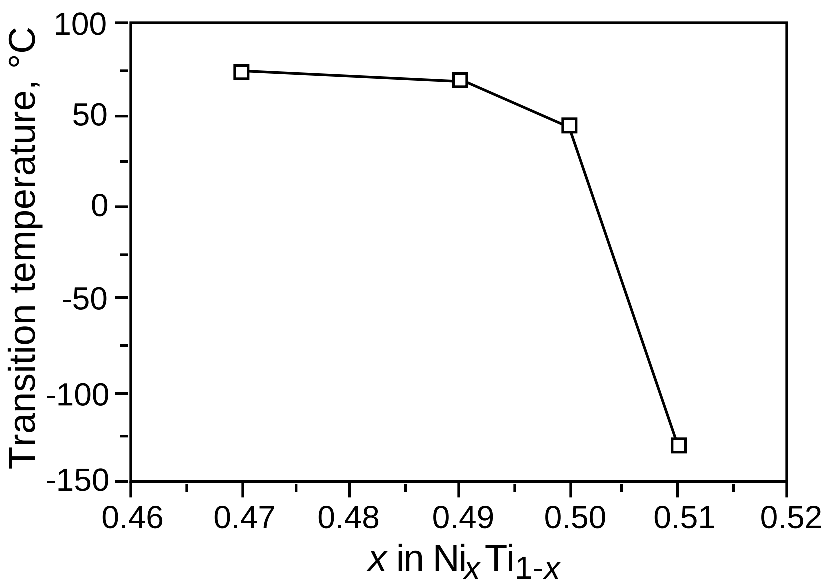

Figure 2. The effect of nickel concentration on the transition temperature. Data from a variety of sources using a variety of methods. (Adapted with permission from Murray, J. L. In *Phase Diagrams of Binary Nickel Alloys*; Nash, P. Ed.; ASM International: Materials Park, OH, 1991; p 345.

In general, the transition temperature decreases as the amount of nickel increases. Therefore, depending upon the exact composition of the alloy, a sample of NiTi could exist in either the austenite or martensite phase at room temperature.

Procedure

Wear eye protection.

Physical Properties of NiTi

Warm some water to 50–60 °C. Obtain a piece of NiTi *wire*, and bend it into a new shape. Dip the wire into the warm water. What happens? Try it again after the wire cools. (What happens if you gently try to bend the wire while it is still hot?)

Grasp both ends of the wire. Place the center of the *wire* in the center of a candle flame, and try to bend the wire into a V-shape with the vertex of the V in the flame. Initially the wire will resist bending. However, as it becomes hot, it will deform into a V-shape. When it reaches this point, remove it from the flame immediately. (Do not hold the wire in the flame long enough for the ends of the wire to get hot.) Cool the wire by waving it in the air or blowing on it. After the wire has returned to room temperature, straighten it into a new shape. Dip the wire into warm water. What happens?

Obtain two NiTi *rods*, one in the low-temperature phase and one in the high-temperature phase. Compare the physical properties of the two phases. How are they similar? How do they differ? Gently try to bend each phase. What happens?

Drop each of the rods on your bench top. What do you notice? Can you identify the phase by the sound?

Tie a string around the low-temperature-phase rod, dip it in warm water (50–60 °C) for a few minutes, then quickly remove the rod and drop it on your bench top. What happens and why?

Tie a string around the high-temperature-phase rod, and dip it in an insulated cup containing liquid nitrogen for a few minutes, then quickly remove the rod and drop it on your bench top. **CAUTION: Liquid nitrogen is extremely cold: 77 K = –196 °C = –321 °F. Do not spill it on your skin or clothing. Severe frostbite or freezing of the flesh can occur. Remove clothing that becomes saturated with liquid nitrogen, because the liquid may be held within the spaces in the fabric and thus freeze the skin underneath.** What happens and why? If you wish to try to bend the rod while cold, use a stack of paper towels as insulation. **CAUTION: Do not touch the cold rod with your bare hands, as frostbite may result.**

Determining the Transition Temperature Range of NiTi

Now that you can recognize the two phases of NiTi by their physical properties, estimate the transition temperature for the solid-state phase change. By dropping the rod, monitor the sound of a low-temperature-phase *rod* as it is slowly warmed in a water bath. Plot your data as relative "ring" or "thud" (y-axis) as a function of temperature (x-axis). Then reverse the process by collecting the same data as the rod is slowly cooled in a water bath and plotting on the same graph as before. What is the transition-temperature range for the change from the low-temperature phase to the high-temperature phase? What is the transition temperature range for the change from the high-temperature phase to the low-temperature phase?

As you are designing and performing experiments, you might consider the following points in order to get good results:

a. A beaker resting on a hot plate may not be at the same temperature as the water inside, so both the thermometer and the rod should be suspended in the water. Should the water be stirred? How long should the rod be left in the water to adjust to the temperature of the water bath? How quickly should the rod be dropped once it is removed from the water?

b. The rod should be dropped from a roughly reproducible initial position that is approximately parallel to the surface it will strike and from a height that ensures an easily recognizable sound.

c. You may find it useful to use your high-temperature-phase rod as a reference.

d. To slowly increase the temperature of water in a beaker, the hot plate will need to be on the lowest setting.

e. Recording data every 5 to 10 °C should be sufficient.

Questions

1. a. Draw a curve through the points on your graph that represent the martensite-to-austenite phase transition. Label the phase-transition-temperature range on your graph.

   b. Draw a curve through the points on the graph that represent the austenite-to-martensite phase transition. Label the phase-transition temperature range on your graph.

   c. How does the curve for the martensite-to-austenite phase transition compare to the graph representing the austenite-to-martensite phase transition? Are the curves the same?

2. Compare your phase-transition temperatures with those obtained by other students in the class. How do these values compare with yours? How might you account for any differences?

3. On the basis of the properties of NiTi, list several (at least three) possibly useful applications for this metal. Be creative!