

# Memory Metal

## *Student Materials*

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# Memory Metal

memory metal -

examples: NiTi, Cu-Zn-Al, Fe-Mn-Si, Au-Ca, Cu-Al-Ni, Cu-Al, etc.

smart material-

## Characteristics of NiTi

1.

- "atomic ballet"

- some limits

2.

3. NiTi consists of 2 structures interconverted by changes in temp. or pressure

- between 0-100°C there are 2 phases

1.

2.

(more dense) + energy === (less dense)

Martensite can have \_\_\_\_\_ variants

- flexibility of martensite due to variants in structure & ability to re-orient these variants = mechanical flexibility

Nickel-Titanium = Nitinol = \_\_\_\_\_  
- nitinol discovered in 1965

- contains nearly equal amounts of \_\_\_\_\_ & \_\_\_\_\_ atoms

NiTi common composition but relative amounts of Ni & Ti varied to control temp. of the phase change responsible for its smart behavior



ex. Ni<sub>0.5</sub>Ti \_\_\_\_\_ Ni \_\_\_\_\_ Ti<sub>0.7</sub>

BB board analogy

-case = \_\_\_\_\_, BB's = \_\_\_\_\_

-groups of atoms = small groups with regular internal pattern separated from each other by gaps

-gaps = \_\_\_\_\_

Nitinol composed of 3-D crystalline regions = \_\_\_\_\_

- grains have random shapes, sizes, orientations

heat to 500-550°C to fix shape, linear defects are minimized, not eliminated

-defects minimized by atoms moving & reshaping grains

-allows atoms to fit closer together

\_\_\_\_\_ -study of the structure of crystals, including ways of describing the crystal structure, the principles that govern the various structures, & methods of determining a crystal's structure

3 parts to crystallography

1.

2.

3.

\_\_\_\_\_ -an imaginary box that can be constructed from arrays of atoms, ions, or molecules-basic unit of a crystal structure

valid unit cells-used to represent the array

Note: Each unit cell contains 1 complete circle, & only the shaded portion of the circle lies in the unit cell.  
If any of the unit cells is moved along its edges the entire pattern is produced.

Simple Cubic

Face-centered cubic

Body-centered cubic

valid unit cell vs. invalid unit cell

coordination number - \_\_\_\_\_

Thermochemical equation to represent transition between phases

martensite + energy  $\rightleftharpoons$  austenite

-energy of a few kJ/mol to change from martensite to austenite

Ni & Ti atoms within the grain(crystalline region) in a sample of memory metal in austenite phase are almost perfectly arranged with few imperfections

-memory from defects in \_\_\_\_\_ phase & grain boundaries

-to give metal a new shape, new defects must be created - goes to new set of defects, rather than old

-new defects obtained by heating metal 500° C while securing shape

-thermal energy allows atoms to relax into lower energy positions = \_\_\_\_\_ formed

-if heated too long, memory metal feature of wire destroyed because if atoms around defects have enough energy they relax & a defect free structure results

-defects created in \_\_\_\_\_ phase (altered by candle flame) create new memory by forcing groups of atoms to have particular positions relative to one another

### Uses and Capabilities

-sense changes in environment & respond to disturbances in a pre-programmed way so used for...

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1. high temp. phase

2. rigid/hard

3. symmetrical

4. ring

5. uniform structure allows sound waves to travel through it easily

6. less dense

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1. low temp. phase

2. flexible

3. less symmetrical

4. thud

5. boundaries between regions with different orientations reduce vibrations & muffle the sound

6. more dense

\_\_\_\_\_ Effect - the phase changes in the 2 directions do not have the same temperature dependence- phase change from austenite to martensite occurs over a lower temp. range than that from martensite to austenite

Graph of figure 9.9 from Companion

Explanation: one solid phase needs to grow within the region of the other-elastic strain in region around new crystal growth

Overall effect: displacement of heating curve to higher temps.  
therefore, whether it was heated or cooled makes a difference

\_\_\_\_\_ - system in which the rates of forward & reverse processes are equal  
-processes can be chemical or physical

-system must be closed

closed vs. steady state

\_\_\_\_\_ - when a system at equilibrium is subjected to a stress (change in temperature, pressure, concentration), the equilibrium will shift in the direction that tends to counteract or relieve the stress

Straining material causes NiTi to change from one phase to another

-as rod is bent some atoms compressed & some pulled apart

Figure 9.7 from Companion

-therefore, pressure exerted on atoms

-material favors martensite (more dense phase) formation under high pressure

Transition temperature (TTR) -

## INVESTIGATION 1

### PURPOSE

To investigate the piece of wire that has been provided by your instructor. Everyone thinks of himself or herself as a good observer. Yet there is much more to being a good observer than meets the eye! It takes concentration, alertness to detail, ingenuity, and often, great patience. It even takes practice! As you make your observations, keep an open mind and also consider any conditions during the experiment that may be important to its outcome. Can any of these conditions be controlled?

### PROCEDURE

- a. Observe the piece of wire that has been provided by your instructor. Note its outward characteristics, especially its shape. (Draw its initial shape in your notebook.) Fill a 400 mL beaker  $\frac{2}{3}$  full of tap water and place it on a wire screen on a ring stand or a hot plate as directed by your instructor. NOTE: Your instructor may provide you with hot water.
- b. Make several coils in the wire by wrapping it around your pencil several times.
- c. If you are to heat water, place the wire into the beaker and begin slowly heating the water while carefully observing the wire. Stop heating after any significant changes to the wire have been observed.
- d. Record your observations.

### FOLLOW-UP QUESTIONS

1. List your observations before and after deforming the wire. Also list your observations as you heated the wire. Specifically, what happened when the deformed wire was exposed to hot water?
  
  
  
  
  
  
  
  
  
  
2. What questions came to mind as you performed this experiment? Invariably, good observations lead to many questions; recall what being a good observer entails.
  
  
  
  
  
  
  
  
  
  
3. Why do you think these wires fall into a category called “smart materials”?
  
  
  
  
  
  
  
  
  
  
4. What possible uses could materials similar to these have?

## INVESTIGATION 2

### PURPOSE

To construct portions of extended three-dimensional solids; to identify unit cells and determine the number of atoms in each cell; to determine the coordination number (number of nearest neighbors) in each of several different structures; to relate structure to some physical properties.

### INTRODUCTION

A crystalline structure consists of a repeating arrangement of atoms, molecules, or ions. In this experiment we will use the ICE Solid-State Model Kit. You will study some of the ways that the building blocks of matter can be packed to form some typical crystals as well as two specific arrangements that are unique to the wire that you researched in Investigation 1.

A useful way of describing the basic pattern of an extended structure is to imagine a three-dimensional, six-sided figure having parallel faces that encloses only a portion of the interior of the extended structure. A cube is the simplest of these “unit cells” and will be used in this investigation. If the proper unit cell is selected, then when it is moved along any of its edges by a distance equal to the length of that edge, it should generate an identical unit cell. Repetition of this process will generate the entire structure of the crystal.

### PROCEDURE

#### PART 1: General Considerations.

Determine how many larger spheres you can pack around a marked sphere in the same plane. [It may be easier to hold the spheres in the palm of your hand while doing this.](#) If all the spheres are the same size does the coordination number depend on size? What if the central sphere is smaller? Larger? Check your predictions.

#### PART 2:

This part of the investigation requires that teams work together, using the Solid State Model Kits or following alternate procedures outlined by your instructor. Each team will build one of the following structures. All teams will then compare and contrast their structures and together answer questions.

Team A: Following the instructions in the kit, assemble the Simple Cubic Structure.

Team B: Following the instructions in the kit, assemble the Body Centered Cubic Structure.

Team C: Following the instructions in the kit, assemble the CsCl Structure with the Cl atoms at the corners.

Team D: Following the instructions in the kit, assemble the CsCl Structure with the Cs atoms at the corners.

Team E: Following the instructions in the kit, assemble the Austenite Structure.

Team F: Following the instructions in the kit, assemble the Martensite Structure.

## FOLLOW-UP QUESTIONS

1. For each structure complete the table below, indicating HOW MANY SPHERES LIE WITH THEIR CENTERS AT THE \_\_\_\_\_ OF THE UNIT CELL.

Structure	Corners	Edges	Faces	Inside
<b>A</b>				
<b>B</b>				
<b>C</b>				
<b>D</b>				
<b>E</b>				
<b>F</b>				

2. With how many other unit cells are the spheres at the \_\_\_\_\_ of the cell shared?  
 a) corners \_\_\_\_\_ cells      b) edges \_\_\_\_\_ cells      c) faces \_\_\_\_\_ cells
3. What fraction of each sphere lying with their center at the \_\_\_\_\_ is part of that cell?  
 a) corner \_\_\_\_\_      b) edge \_\_\_\_\_      c) face \_\_\_\_\_
4. For each structure complete the table below, indicating HOW MANY TOTAL SPHERES OCCUPY EACH SITE.

Structure	Corners	Edges	Faces	Inside	Total in Cell
<b>A</b>					
<b>B</b>					
<b>C</b>					
<b>D</b>					
<b>E</b>					
<b>F</b>					

5. Compare the models of austenite and martensite.
- a) What packing arrangement is used in the austenite structure? \_\_\_\_\_
- b) How is the austenite structure altered to yield the martensite structure? \_\_\_\_\_
- c) Compare the number of spheres per unit cell for each structure. How does the density of martensite compare to that of austenite? \_\_\_\_\_
- d) From what you have learned about these structures, which do you think would be the more flexible low temperature phase of the wire in Investigation 1? Explain.



## INVESTIGATION 4

### PURPOSE

To investigate some of the mechanical properties of the two phases of the NiTi alloy and to relate these properties to the structures of these phases.

### PROCEDURE

#### Part I

- a. Try gently bending each of the two rods provided by your instructor into a V-shape. Identify the rod that is inflexible.
- b. Cool the less flexible rod in liquid nitrogen or an alternative cooling bath (CAUTION), as directed by your instructor. Use tongs and gloves.
- c. Remove the rod from the liquid nitrogen or alternative cooling bath. Then, while wearing gloves, bend the rod into a V-shape.
- d. Allow the rod to warm back to room temperature.

#### Part II

- e. Warm the flexible rod in water that has been heated to near the boiling point. Remove with tongs, and, while wearing gloves, try to bend it.
- f. Allow the rod to cool and then try to bend it again.

#### Part III

- g. Using the appropriate methods, return both rods to their original linear shapes.
- h. Try scratching each rod with the other.

### FOLLOW-UP QUESTIONS

1. State your observations for step (a) of the procedure.
2. State your observations for step (d) of the procedure.
3. State your observations for step (e).
4. State your observations for step (f).
5. State your observations for step (g).
6. State your observations for step (h).

7. Based upon your observations, which rod was in the low temperature martensite phase and which was in the high temperature austenite phase?
  
8. a) Which rod was harder than the other?  
  
b) Is this consistent with your answer to question (5)? Explain.
  
9. If you were to make a pair of eye-glass frames that could be easily restored to their original shape if accidentally sat upon:
  - a) In which phase would you manufacture them?
  
  - b) Where would you adjust the transition temperature- above or below room temperature?
  
  - c) If your glasses were bent, what, if anything, would you do to return them to their original shape? Explain.
  
  - d) What if they didn't fit exactly right? What would you need to do to adjust them?

## INVESTIGATION 5

### PURPOSE

To investigate the acoustic properties of the two rods that you used in Investigation 4.

### PROCEDURE

- a. Determine which of the rods is in the martensite phase (recall Investigation 4).
- b. Using the rod that you selected in (a), tie one end to a string and suspend it in a beaker of water on a hot plate by tying the other end of the string to a ring on the stand at the appropriate height. After several minutes, remove the rod and drop it on the counter-top from a height of 50 cm. The rod should be held parallel to the counter as it is dropped. Note the nature of the sound that the rod produces (thud, ring, intermediate). Record the temperature of the water.
- c. Return the rod to the beaker, and turn on the hot plate at its lowest setting. Remove and test the rod at approximately 10 °C intervals. Continue until a noticeable change in sound is detected.
- d. Repeat the above procedure until the water cools to just above room temperature.

### FOLLOW-UP QUESTIONS

1. How did you decide which rod was martensite?
2. Describe the changes in sound produced as the rod was slowly heated.
3. Do the sounds produced at each temperature depend upon whether the rod is being heated or cooled?
4. How do you account for this observed change in sound?

## EXPERIMENT 1

### PROBLEM

Determine the Transformation Temperature (TTR) for your sample of shape memory metal.

### PROCEDURE

Think about the investigations you have worked on in this unit and use what you have learned to devise your own procedure. There are many ways of doing this. You should consider the scientific method as you proceed to help you formulate your thoughts. **Be sure that your procedure has been approved by your instructor before you begin.**

### DATA

Dependent upon procedure.

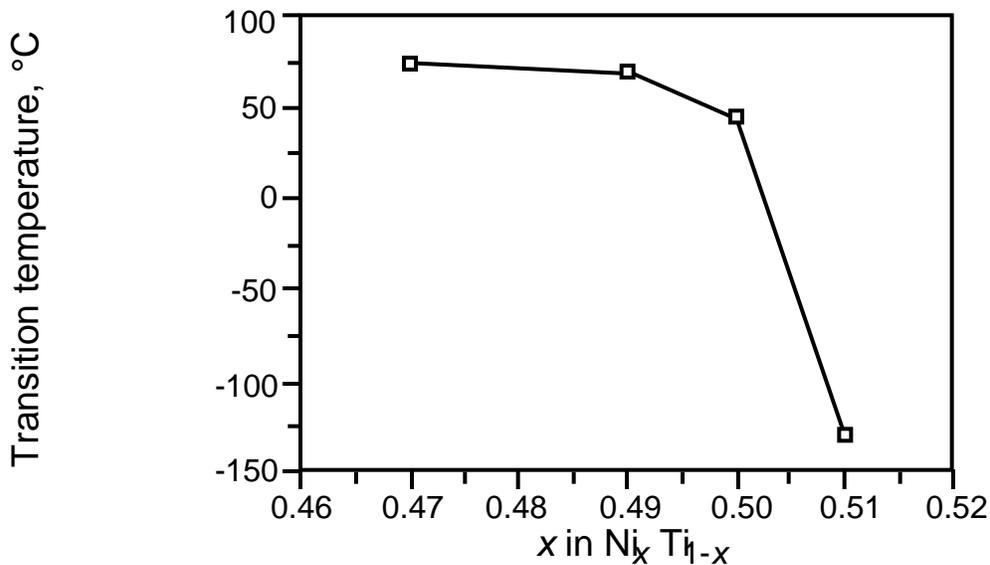
### ANALYSIS

### CONCLUSION

TTR

### EXTENSIONS

Based upon the graph below, estimate the composition of your sample.



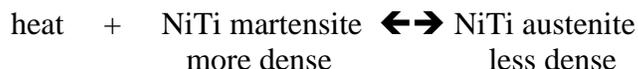
Suggest some possible uses of shape memory metals; don't just list those that you know already exist, but also think about some that may not yet exist, but would be really useful if they did.

Do TTR's change if the sample is repeatedly deformed. If so, how? Why?

How quickly does the shape change as a function of temperature?

## Memory Metal Review Questions

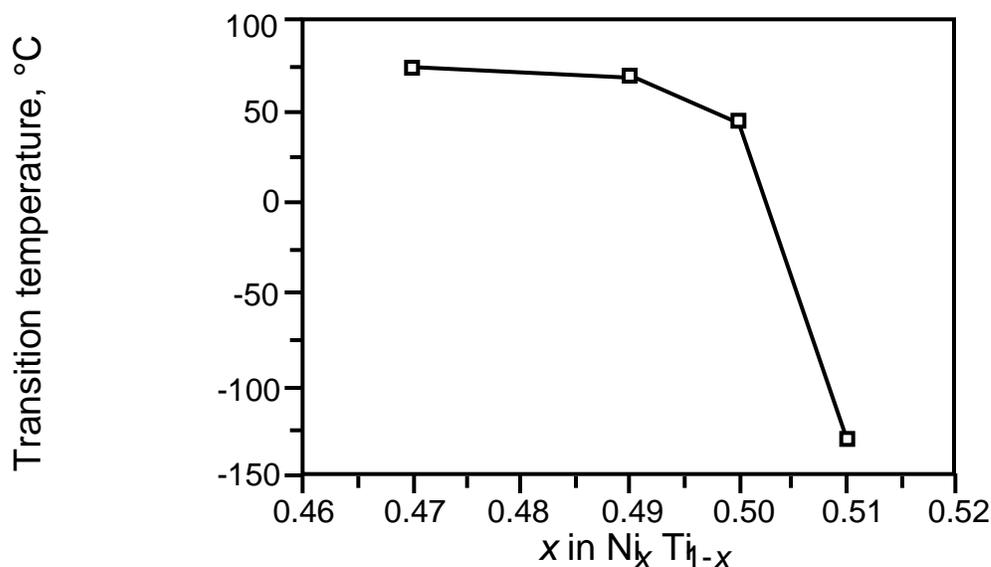
1. One of the problems with syringes used in some chemistry experiments is that the metal plunger can bend, making the expensive syringe useless. To eliminate this problem, a company has recently produced a syringe whose plunger is made from memory metal, NiTi. Recall the equilibrium for this material:



Based on temperature and/or pressure effects associated with this equilibrium, design such a plunger: Specifically, how is its operation connected to the equilibrium, and what instructions, if any, would you need to give the purchaser?

2. Sarah Mason's recently published mystery thriller, "Dying Breath," describes a knife that could be fashioned from memory metal. The following graph shows the transition temperature of the phase change of memory metal as a function of its composition, i.e.,  $x$  in the formula  $\text{Ni}_x\text{Ti}_{1-x}$ .

The Effect of Ni Concentration on the Transition Temperature



This figure was adapted from *Teaching General Chemistry: A Material Science Companion*. It is a compilation of data by several researchers, who measured the composition and transition temperatures by different methods.

a. If the villain desires the knife to be in the low-temperature phase at room temperature (about 25°C), select a value of  $x$  that will produce this result and explain your choice.

b. The villain has designed the knife's initial shape to leave an unusual imprint when it is used for the crime. The knife is subsequently to be bent into a different shape at room temperature, so that it appears that the knife could not have caused the imprint. Would hot water (50°C) or candle flame temperature (500°C) have been required to give the knife its initial, unusual shape and does this temperature correspond to a phase change of the Ni and Ti atoms; or to movement of defects in the alloy and why?

c. If you were the investigator assigned to the case, how would you change the temperature to cause the knife to recover its initial, unusual shape, and does this temperature correspond to a phase change of the Ni and Ti atoms; or to movement of defects in the alloy and why?

3. When a NiTi rod is heated into its symmetric high temperature phase from the less

symmetric structure of its low temperature phase which of the following is true?

- a. it becomes more flexible and thuds when dropped
- b. it becomes more flexible and rings when dropped
- c. it becomes more rigid and thuds when dropped
- d. it becomes more rigid and rings when dropped

4. A sculpture made of memory metal is found to change its shape when electricity is passed through it because

- a. it is cooled into the low-temperature martensite phase
- b. it is heated into the high-temperature austenite phase
- c. passing electricity through the structure changes its atomic composition
- d. passing electricity through the structure removes electrons from the structure

5. Which of the following phase changes will release heat?

- a. melting an alloy
- b. transforming NiTi memory metal from the phase that thuds to the phase that rings when dropped
- c. subliming dry ice into the gas phase
- d. condensing gaseous water into liquid water

# Memory Metal Assessment

Name \_\_\_\_\_

Date \_\_\_\_\_ Hour \_\_\_\_\_

## Matching

Match the word with the best definition.

- |       |                             |   |
|-------|-----------------------------|---|
| _____ | 1. austenite                | a. a pattern that can be shifted repeatedly to create the entire structure of atoms in a crystal                        |
| _____ | 2. martensite               | b. a solid solution composed of two or more metals  |
| _____ | 3. transition temperature   | c. alloy containing nearly equal amounts of nickel and titanium   |
| _____ | 4. Nitinol                  | d. a physical state of matter   |
| _____ | 5. alloy                    | e. a type of unit cell  |
| _____ | 6. smart material           | f. a substance that can respond to stimuli in its environment   |
| _____ | 7. density                  | g. high temperature phase   |
| _____ | 8. unit cell                | h. low temperature phase  |
| _____ | 9. coordination number      | i. the temperature at which a phase transformation occurs   |
| _____ | 10. body-centered cubic     | j. mass per unit volume   |
| _____ | 11. phase                   | k. number of nearest neighbors  |
| _____ | 12. LeChatelier's Principle | l. when a system at equilibrium experiences a stress, the equilibrium shifts partially to relieve that stress partially |
|       |                             | m. the temperature at which martensite melts  |

## Multiple Choice

Choose the best answer.

- \_\_\_\_\_ 13. In the high-temperature phase of NiTi, the coordination numbers of the Ni and Ti are
- 6 for Ni and 6 for Ti
  - 6 for Ni and 8 for Ti
  - 8 for Ni and 6 for Ti
  - 8 for Ni and 8 for Ti
- \_\_\_\_\_ 14. What technique lets us determine the atomic positions in NiTi memory metal both before and after the solid has undergone its phase change?
- spectroscopy with visible light
  - measurement of specific heat
  - electrical resistivity
  - x-ray diffraction
- \_\_\_\_\_ 15. Austenite exhibits which characteristic?
- less symmetrical than martensite
  - more rigid than martensite
  - more flexible than martensite
  - both a and c
- \_\_\_\_\_ 16. At room temperature Nitinol can exist in either of two structures, which are dependent upon
- the mass of the sample.
  - the exact ratio of Ni to Ti.
  - the length of the sample.
  - the diameter of the rod.
- \_\_\_\_\_ 17. In some phase changes like that of ice and water, there is a noticeable change; however, there is no visible phase change between austenite and martensite because
- it only occurs at the atomic level.
  - only two atoms exchange places.
  - the structures are the same
  - the temperature is too high
  - no phase change occurs.

## Problems

18. Using [figure 9.10](#) [put this figure in](#), what compositions of  $\text{Ni}_x\text{Ti}_{1-x}$  would you choose so as to have two samples, one of which is in the low-temperature phase at 0 °C, with the other in the high temperature phase at this same temperature. How could you tell them apart without chemical analysis?

