

# Nitinol Demo

## "Memory" Metal

Nitinol is a shape memory alloy that exhibits a solid state phase change with interesting and useful properties.

Ni = nickel

Ti = titanium

NOL = Naval Ordnance Laboratory

Straighten or deform a piece of shape memory metal. Dip the distorted wire into a beaker of water at approximately 70°C (or higher based on which alloy you have). It will return to its original "trained" shape. Test different samples and shapes. A hair dryer may also be used as a source of heat. Hold the metal in the warm water using pliers on each end. Deform the metal and release the wire from one of the pliers - it will be elastic and not pliable.

Straighten or attempt to deform a piece of super-elastic metal. It springs back to its original shape. Dip the super-elastic metal into a dry ice/ethanol bath and immediately straighten or deform the metal upon removal - it will now relax and deform. It will return to its original shape as it warms in the air.

A solid state phase change occurs at a specific transition temperature. A crystal structure change occurs - more pliable structure at cooler temperatures and an elastic structure at warmer temperatures. By varying the percentages of nickel and titanium in the alloy, different transition temperatures can be achieved.

Shape memory wire - transition above room temperature

Super-elastic wire - transition below room temperature

The "set" shape of a piece of nitinol can be changed by using a heat treatment around 500°C.

ChemMatters has a great article on nitinol called "Memory Metal" in the October 1993 issue. Have the students read the article in class and answer questions such as the following in their journal:

1. Title of article
2. Date of article
3. Name the 2 crystalline structures that nitinol forms.
4. List 4 uses of nitinol.
5. Think of a possible new use of nitinol - something not mentioned in the article. Bonus

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#### Sources of nitinol:

Flinn Scientific

Catalog number AP1937

[www.flinnsci.com](http://www.flinnsci.com)

1-800-452-1261

Chem Fax with additional information on shape memory alloys is included

Educational Innovations

Catalog number: HS-6 by the foot HS-9 package of ten 3" pieces

[www.teachersource.com](http://www.teachersource.com)

1-888-912-7474

Includes background information and directions for retraining the metal into a new "set" shape.

#### Websites

<http://www.nitinol.com>

click on "engineering" for lots of info

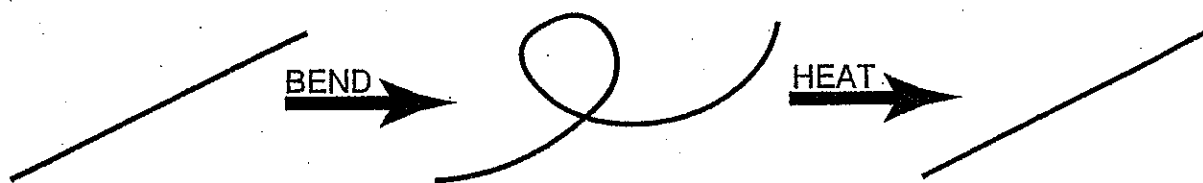
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<http://www.imagesco.com/catalog/nitinol/nitinol.html>

<http://www.memry.com/nitinolfaq/nitinolfaq.html>

great!!!!!!!!!!

Nitinol memory metal has two crystalline phase forms with a transition temperature between 30° and 50°C. At high temperature the NiTi alloy prefers the Austenite phase while at low temperature, the alloy prefers the Martensite phase. Because the Martensite phase crystal structure consists of a series of planes which may be displaced, it can be deformed. The Martensite structure has 24 different variants to carry out this transformation and, as a result, can be deformed in nearly any direction. When the alloy is heated to the Austenite phase, the planes are slid back into place and the structure reverts to its original form. Thus, the metal appears to 'remember' its original shape.



### DEMONSTRATION #1

#### *Memory Metal Remembers its Austenite Shape*

1. Place a sample of NiTi wire on an overhead projector and examine its shape.
2. Bend or coil the wire and return it to the stage of the projector. You may want to fasten one end of the wire with a piece of transparent tape.
3. Heat the wire with a hair dryer and watch it straighten out as it returns to the preferred higher temperature Austenite phase.
4. Alternatively, the bent NiTi wire sample can be dropped into a projected petri dish containing hot water.
5. Still another variation of this demonstration uses resistive heating to change the NiTi wire to its Austenite phase. Simply connect each end of a short sample wire to a 9 volt battery (2 D-cell batteries in series may be substituted) for a few seconds. As the wire resistively heats, it returns to its Austenite phase.

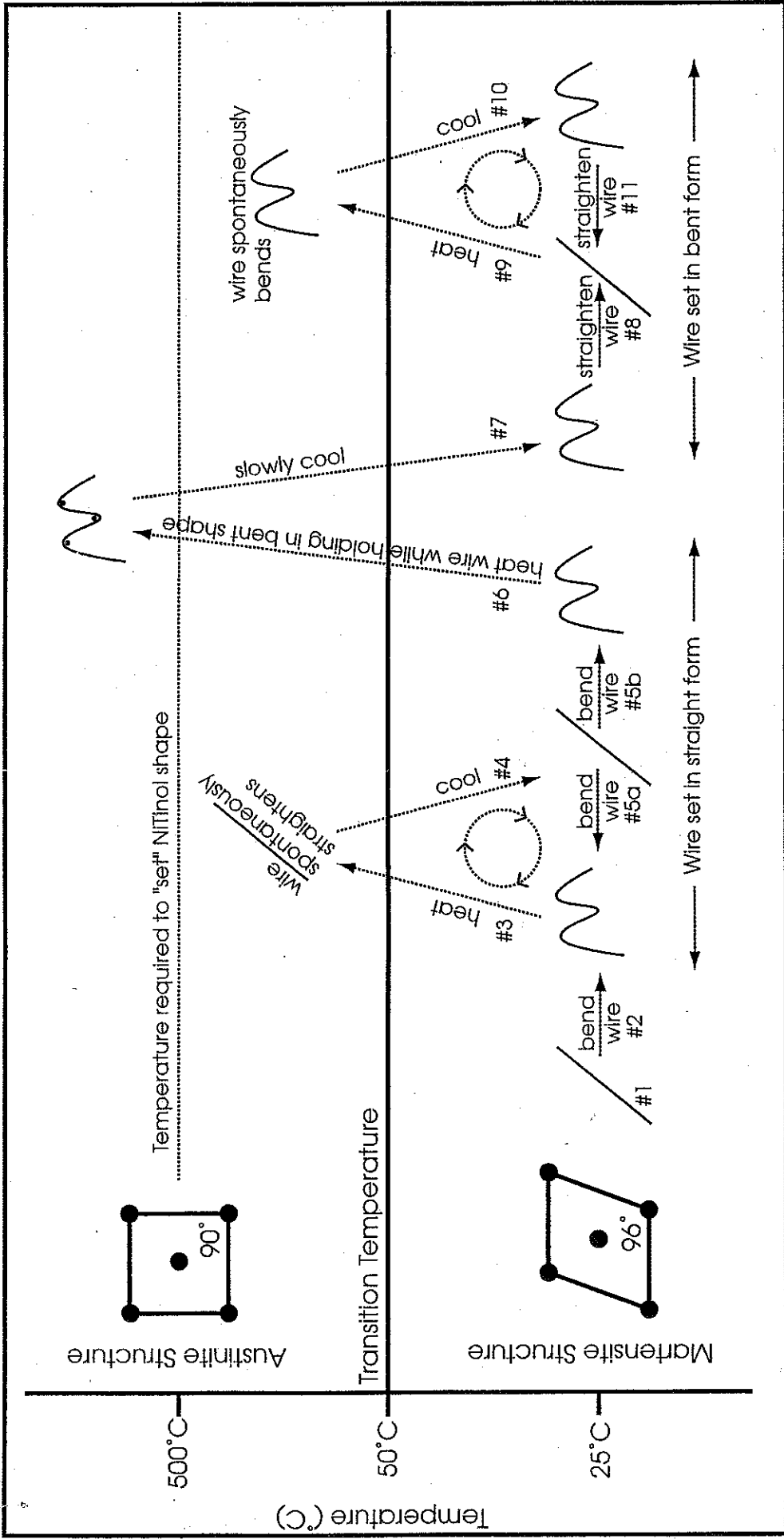
### DEMONSTRATION #1

#### *Setting NiTi Wire into a New Shape*

1. Place a sample of NiTi wire under tension by bending it and hold so that the wire maintains its bent shape.
2. Holding the wire carefully so as not to burn your fingers, bring the bent end of the NiTi wire *close* to a candle or Bunsen burner flame. Heat it slowly until you feel a release of tension. At that point, remove the wire from the vicinity of the flame. Note do not heat the wire more than is necessary to release the tension.
3. Let cool. The NiTi wire has now been set into a new shape.
4. Repeat demonstration #1 to show that heating the wire will now cause it to return to its new bent shape.

Nitinol 'memory' wire is available from Educational Innovations in two forms:  
 1. 3" samples sold in packages of 10. ITEM HS-9  
 2. Longer lengths which are sold by the foot and are considerably larger in diameter (~.030"). ITEM HS-6

# Mechanics of the Nitinol Shape Memory Effect



The wire is usually purchased "set" straight (step #1). Below the transition temperature, the Marstenite form of the wire can be bent quite easily (step #2). When heated to the transition temperature (step #3), the unit cells change to the Austinite form and its originally "set" shape. The cycle (steps #4, #5a and #3) can be repeated many times. To "set" the wire into a new shape, heat it to 500°C while restricting its movement (steps #5b, #6, and #7). The new cycle (steps #8, #9, #10, and #11) can be repeated many times.

# Memory

Three years ago, Los Angeles Dodgers pitcher Orel Hershiser suddenly found his brilliant career threatened by severe shoulder problems. After seven years of major league pitching, Hershiser had torn the tissue and tendons in his shoulder so badly that his arm was no longer fixed firmly in the socket. Every time he hurled the ball, he felt more pain and lost more control. The problem had put many a pitcher before him out of business.

But thanks to Nitinol, a strong and flexible nickel-titanium alloy, Hershiser was out only one season and steadily regained most of his original power. Orthopedic surgeons drilled a hole in his shoulder bone and inserted a tiny metal anchor that wedged itself into the hole by the action of a Nitinol hook. Sutures tied to the metal anchor allowed the surgeons to firmly reattach the tendons to bone.

Nitinol can straighten teeth and intercept blood clots. Eyeglass frames constructed of Nitinol can weather severe abuse (you can twist them, sit on them, and otherwise torture them) and they will spring back to their original shape.

Recently, a NASA engineer devised a pair of automatic Nitinol tweezers that are expected to be useful to doctors who must extract minute objects through small incisions.

## A lot of work and a little luck

Just where did Nitinol come from and, more importantly, how was its ability to remember and return to a predetermined shape discovered? In the late 1950s and early 1960s, William J. Buehler, a researcher at the Naval Ordnance Laboratory in White Oak, Maryland, was looking for a fatigue-, impact-, and heat-resistant alloy (a sub-

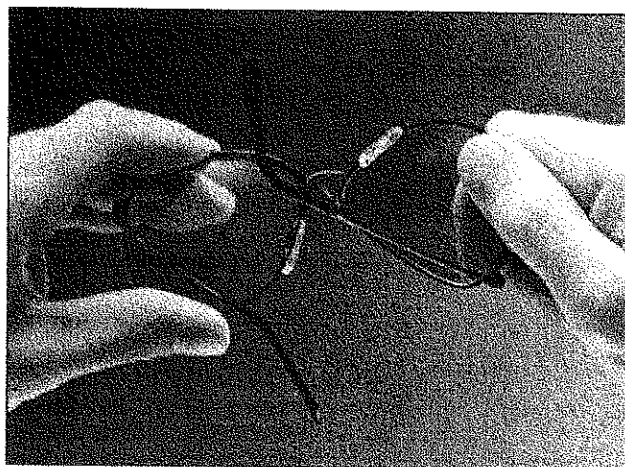
stance composed of two or more metals) to use in the nose cone of a Navy missile. One of the alloys he investigated was an equiatomic (50%–50%) mixture of nickel and titanium, which exhibited the qualities Buehler desired. He named his discovery Nitinol (*Nickel Titanium Naval Ordnance Laboratory*). Buehler made up long, thin strips of Nitinol to use as "props" in demonstrations for his superiors at the laboratory. He would bend the strip into short folds longitudinally, forming a sort of metal accordion. The strip was then bent and stretched (as an accordion) to show that it wouldn't break. At a routine laboratory management meeting in 1961 an accordion-folded, fatigue-resistant strip of Nitinol was passed around a conference table and flexed repeatedly by all present. One of the Associate Technical Directors, the late Dr. David S. Muzzey, heated the compressed Nitinol strip with his pipe lighter. To the startled amazement of all, it stretched out to its original shape!

## The secret of a good memory

What made Nitinol remember its shape? To help get the answer to that Buehler asked Dr. Frederick E. Wang, an expert in crystal physics, to join his research team. It was Wang who discovered the atomic structural changes that endowed the alloy with its unique characteristic.

Phase changes between solids and liq-

uids (melting or solidifying) or liquids and gases (vaporization or condensation) are well known. Less well known, however, is the fact that such changes can occur when both phases are solids. Such phase changes involve the rearrangement of the position of particles (atoms, molecules, or ions) within the crystal structure of the solid. To fix the parent shape (the shape to which you will want Nitinol to return) the Nitinol must be held in the parent position and heated to about 500 °C (932 °F). There is no visible change in the shape of the metal; all the



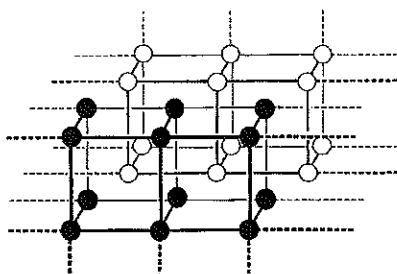
These expensive glasses were twisted like a pretzel. Who would deliberately do this? Someone who had Nitinol wire frames, which snap back to a proper fit even without being heated. The frames spring back instantly because they are made of a Nitinol alloy whose critical temperature is well below room temperature. This means that the alloy is always in the return-to-memorized-shape mode and, therefore, behaves like a super-elastic spring. Similar alloys are used for the wires in dental braces and surgical anchors, which cannot be heated after insertion.

# METALS

by George B. Kauffman  
and Isaac Mayo

changes occur at the atomic level. Nitinol metal is a conglomeration of crystals of random size, shape, and orientation. When Nitinol is heated to the high temperature, the thermal energy causes the atoms to arrange themselves into the most compact and regular pattern possible. The Nitinol crystals take on a cubic arrangement called the austenite phase (see Figure 1).

When Nitinol wire cools below a certain



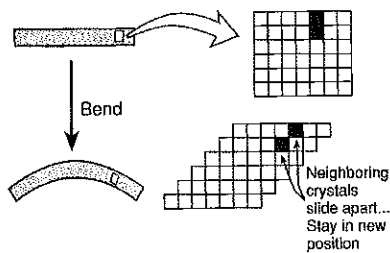
**Figure 1.** The austenite phase of Nitinol. Nickel atoms (white) are positioned at the corner of a cube that has a titanium atom at its center. The titanium atoms (black) form their own cubes that interlock with the nickel cubes. Each Ni atom is in the center of a Ti cube and vice versa.

DAGMAR: MEMORY METAL INSTITUTE FOR CHEMICAL EDUCATION

## Crystals with good neighbors

A metal object begins as a hot, molten liquid. As the liquid cools, a few atoms attach to each other in a geometric pattern, and this minute solid grows as other atoms cool and join. Because these solid crystals start at many locations, they grow until they eventually bump into other crystals. The boundary, where neighboring crystals meet, is not as strong as the crystal itself. When a metal bends or breaks, it is because the crystal boundaries slide or rupture. Metallurgists are constantly seeking to strengthen these boundaries.

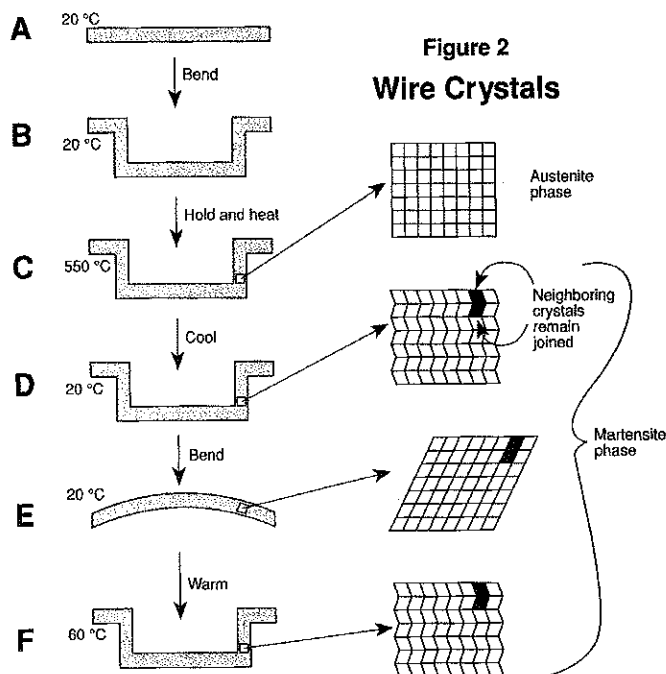
When you bend ordinary metal—such as the iron in a coat hanger—neighboring crystals slide past each other and then stay in their new positions.



Nitinol's unusual behavior is due to the fact that, when it is bent, each martensite crystal can deform to relieve the strain instead of sliding at the crystal boundaries.

In steps A, B, and C, the Nitinol wire is treated at high temperature to set the parent shape. When it is cooled, D, the

phase changes from austenite to martensite. Because martensite crystals are slightly flexible, they can deform to accommodate bending of the wire, E, while remaining attached to neighboring crystals. When warmed, F, the martensite crystals revert to their undeformed shape, and the wire magically unbends.



### A. Before Surgery

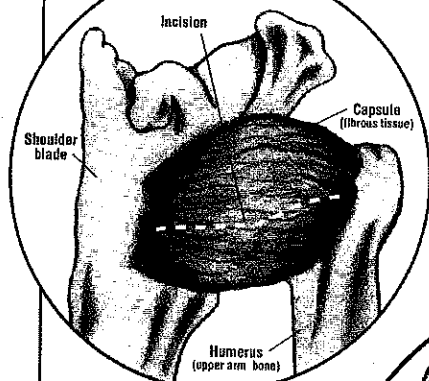
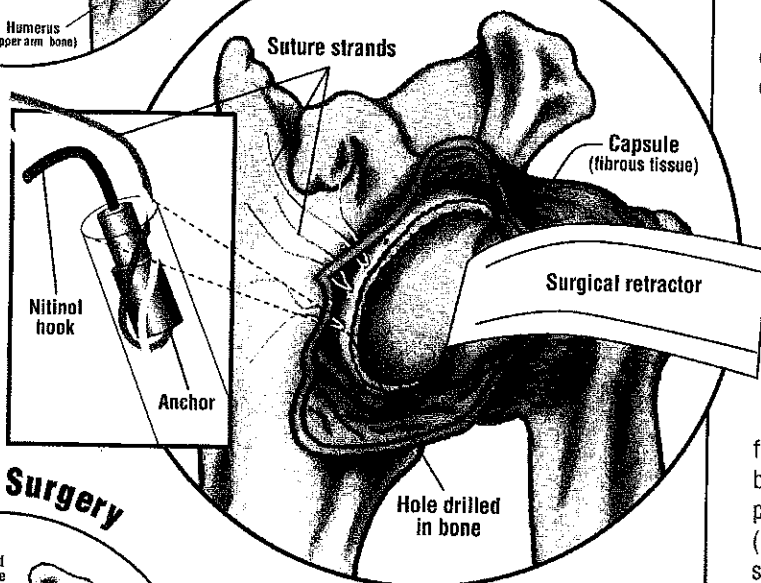
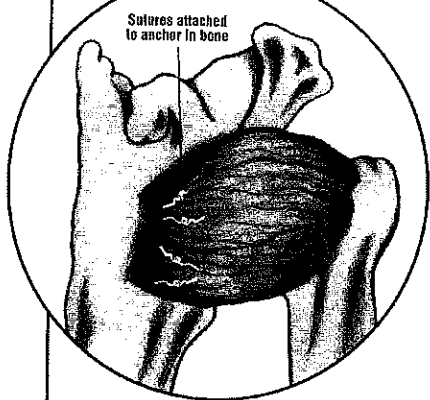


Figure 2. In Orel Hershiser's injury, one of the three ligaments that comprise the capsule, illustration A, was pulled from the bone. To heal properly, the ligament must be held tightly in place. A hole was drilled in the bone and an anchor composed of a titanium body and a Nitinol hook was inserted. When the surgeon pulled on the sutures attached to the anchor, the springy hook was set in the

### B. During Surgery



### C. After Surgery



porous bone, B. The sutures were threaded through the capsule, then tied together to hold the ligament firmly against the bone. The sutures eventually dissolved, but the anchor remained embedded in the bone. Prior to the invention of the Nitinol anchor, sutures were held by screws or staples (about 50 times larger than the Nitinol anchor), or by being threaded through a hole drilled completely through the bone.

mal motion of the atoms increases and the atoms bump and push away from one another. At 43 °C the crystals are strained and, to relieve this strain, they revert to their austenite configuration, which restores the parent shape of the metal. As the tweezers tips change from the open (deformed) state to the closed (parent) state, they grab the object firmly, making it easy to remove.

### What's Nitinol good for?

Once some early manufacturing problems had been solved in the late 1960s, the military began to use Nitinol couplers to join hydraulic lines in F-14 fighter planes. When cooled in liquid nitrogen the couplers expand to a large inner diameter, making them easy to slip over the hydraulic lines to be joined. On warming to room temperature, the coupler shrinks with great force to form a totally sealed joint. These couplers are still being used in the F-14 today.

The health profession is using Nitinol to simplify and remove risk from previously dangerous procedures, as illustrated by the Hershiser surgery.

Cardiovascular surgeons often implant wire filters (which resemble birds' nests) in the bodies of patients who are prone to develop potentially fatal pulmonary embolisms (blood clots). At one time this was a major surgical procedure, involving large incisions. Now, by using Nitinol, a surgeon can deform the birdnest-shaped filter into a bundle of wires that can be inserted to the proper position through a catheter in the patient's vein. When released from the catheter, the bundle of wires springs back into its original birds' nest shape, ready to trap any blood clots. The patient, who required only local anesthesia, can go home the same day.

Do you wear braces? If the orthodontic wire in your mouth is Nitinol, you probably need to go to the orthodontist for readjustments far less often than a friend who wears the old-fashioned stainless steel braces. Your braces tend to remember their parent shape and, as your growing teeth deform them, they are always trying to revert to that shape.

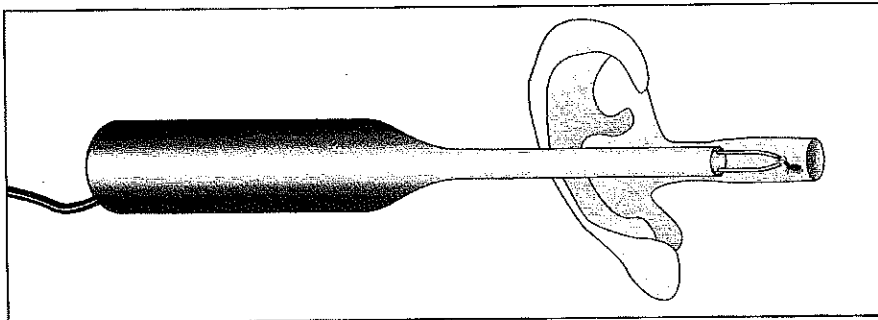
An application of Nitinol with perhaps the greatest consumer appeal is in the manufacture of eyeglass frames. Conventional frames are always loosening, falling down your nose, or getting sat upon. Using Nitinol in the frame's bridge, top bar, and temples allows the frames to return to their parent shape upon warming.

temperature (the transition temperature), the atoms in the crystals rearrange into the martensite phase. (Remember, there is no change at the visible level. The phase change occurs only at the atomic level.)

As the solid changes from the austenite phase to the martensite phase, the atoms within a crystal rearrange into a slightly different three-dimensional shape, though the crystal retains its original neighbors (see box, Crystals with good neighbors).

To see how this happens, let's examine

NASA's Nitinol tweezers, shown in Figure 3. During its manufacture, the alloy's composition (Ni-Ti ratio) was selected so that the transition temperature is 43 °C (110 °F). Before insertion, the Nitinol is in the martensite phase and the tweezers' tip is closed. At room temperature, the doctor bends the tips open, then inserts the tweezers into the ear canal and guides the tip to the foreign object. At the push of a button, electricity flows and the wire quickly warms up to slightly above body temperature. The ther-



**Figure 3:** Automatic tweezers recently invented by NASA engineer Earl Angulo. The tips of the tweezers are made of Nitinol wire that is connected to an electrical circuit powered either by a power supply or by a battery in the handle of the instrument. When current flows, the tips are heated slightly and close on the foreign object.

Nitinol is also used in safety devices because of its unique sensitivity to heat. A Nitinol anti-scalding valve on the market can be inserted into water faucets and shower heads. The springlike apparatus is designed so that if the temperature of the water approaches 120 °F (49 °C) the water flow is automatically shut off. With more than 30,000 people (mostly children) receiving scald burns in the bath and shower every year in the U.S. alone, this device will certainly save a lot of pain and suffering.

Nitinol-based fire sprinkler systems are also available. The response time from fire to water release is significantly reduced from that of the older solder systems.



PHOTO: AMY MEYER PHEER

The Thermobile is a simple loop of Nitinol wire mounted on two pulleys. If one pulley is dipped in hot water, one side of the loop tries to straighten, which makes the tension in the two sides of the loop unequal and spins the pulleys. In addition to being a charming toy, the Thermobile may be the world's simplest heat engine. Researcher Frederick Wang has constructed multiloop engines that produce useful power.

### A toy now, an engine later?

In 1980 Dr. Wang left the military and started his own company, Innovative Technology International (ITI), to manufacture Nitinol and do research into possible applications. In 1985 ITI began marketing a toy called the Thermobile™, constructed of two pulleys and a single piece of Nitinol wire wrapped around the pulleys. One end of the Thermobile is inserted in 75 °C (167 °F) water. The single strand of Nitinol wire, passing through the hot water, contracts and tries to straighten out to its parent shape — a straight wire. The resultant torque forces the two pulleys to rotate. Thus the Thermobile converts heat energy to mechanical energy.

Can this type of system be adapted and used as a clean power source? After all, the resulting torque and force could theoretically generate electricity, turn flywheels, propel an airplane, or power a car. Research and experimentation on Nitinol-based engines is under way. ITI and Wang have designed several prototypes of Nitinol-based engines. Wang has demonstrated 40-watt Nitinol engines with internal hot water reservoirs.

Perhaps one day there will no longer be controversy about supposedly "clean" nuclear power plants; maybe our electricity

### Nitinol sources

Memory Metal is the latest kit produced by the Institute for Chemical Education. It consists of a booklet containing a brief discussion and description of the chemistry of Nitinol's shape-memory retention and about two feet of Nitinol wire in the form of the letters "ICE." You can experiment by deforming the wire and then heating it to above 80 °C (176 °F) to observe the recovery. Memory Metal (order number 91-011A2) is available for \$12 from: Institute for Chemical Education, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396 (Phone: 608/262-3033; Fax: 608/262-0381).

If you would like a Thermobile, send a check for \$22.00 to Innovative Technology International, 10747-3 Tucker Street, Beltsville, MD 20705.

will be generated by Buehler and Wang's incredible alloy. Hey, maybe the fenders of Dad's car will be made of Nitinol. This isn't so far-fetched — research and development on Nitinol car frames is also under way. So you get a little dent in the car? Just apply warm water, and no one, including Dad, will be the wiser.

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MATERIALS AND PROPERTIES FOR

# CORONARY STENTS

*Coronary stents must have excellent mechanical properties to provide strength to artery walls.*

J. Lévesque, D. Dubé, M. Fiset  
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Coronary stents are small metallic tubes implanted in heart arteries to prevent the arteries from closing up. Their principal advantage is that they do not require open-heart surgery, as they are implanted directly through the arteries. More than one million stents are implanted each year in the world, and around 60% of these are in the United States. The world market for stents in 1999 was \$2.2 billion, and it is estimated that in 2006 it will reach around \$3.2 billion.

Over 40 different types of stents are commercially available or in development, and they are made of stainless steel, Nitinol shape-memory alloy, cobalt-chromium alloys, platinum, tantalum, or gold. In the last decade, a large number of patents have been issued, and several papers have been published concerning stents and their properties. Most of these studies focused on material biocompatibility and the reactions between stents and tissues.

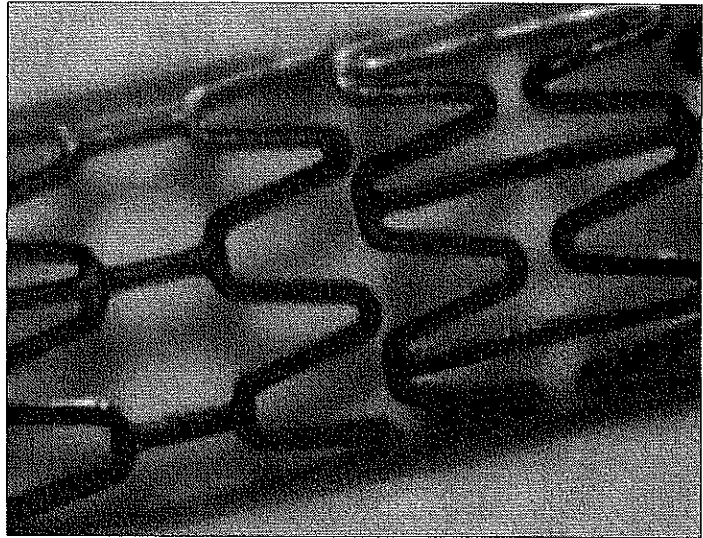
However, even though these are very important aspects to consider, mechanical properties also have to be taken into account. In fact, the main reason for stents is to provide mechanical support to the artery wall. Therefore, inappropriate mechanical properties could lead to complications such as damage to the artery wall.

This review will present the required properties for appropriate stent fabrication, and it will focus on mechanical aspects that have received little attention until a few years ago. Finally, an outlook for the future of materials and properties for stents will be discussed.

## Corrosion processes

Corrosion and its associated products can affect tissues in several ways. First, corroding materials can release metallic ions into the surrounding tissues and these can be toxic to cells, or they can be mutagenic, allergenic, or even carcinogenic. For

\*Member of ASM International



*Most stents are made of materials that do not degrade in the body, such as Nitinol shape memory alloy, stainless steel, or cobalt-chromium. Some new concepts are based on the idea of biodegradable materials such as polymers and magnesium. Photo courtesy Synbiotech Medical Inc.*

example, 316L stainless steel and Nitinol (55Ni-45Ti) contain large amounts of nickel, which is known to be potentially carcinogenic. Stainless steel contains between about 8 and 12 wt% nickel, and Nitinol contains about 55 wt%.

Nitinol owes its good corrosion resistance to a passive surface film consisting mainly of  $\text{TiO}_2$ . The chemical and mechanical stabilities of this film have still not been unambiguously established, especially after the deployment required to expand the stent after its positioning. Even though it has been demonstrated that this oxide layer remains essentially unchanged after implantation, analysis of samples from surrounding tissues from the vascular wall around a Nitinol stent has revealed tiny deposits of nickel and titanium compounds. These deposits are believed to be corrosion products that had undergone phagocytosis, meaning that they have been "captured" by some sort of white blood cells.

Even though it is probable that Nitinol does not (macroscopically) corrode substantially over the human lifetime, nickel compounds certainly diffuse through the passive layer, thus reaching the surrounding tissues. After reaching surrounding tissues, nickel tends to leave the impregnation site and to spread out, probably transported by the lymphatic system. Thus, its potential negative

## Mechanical properties of stent materials

Nitinol owes its good corrosion resistance to a passive surface film consisting mainly of  $TiO_2$ .

Material	Composition, wt%	Elastic modulus, GPa (Msi)	Tensile strength $\sigma_{UTS}$ , MPa (ksi)	Ultimate tensile strength $\sigma_{UTS}$ , MPa (ksi)	Elongation, %
316L stainless steel, annealed	17Cr, 12Ni, 2.5 Mo, <0.03C, balance Fe <sup>a</sup>	193 <sup>b</sup> (28)	260 <sup>a</sup> (38)	550 <sup>a</sup> (80)	50 <sup>a</sup>
Nitinol <sup>c</sup>	55 Ni - 45 Ti	Austenite 83 (12), Martensite 28 to 41 (4 to 6)	Austenite 195 to 690 (28 to 100), Martensite 70 to 140 (10 to 20)	Annealed (130), Work-hardened 1900 (276)	Arnealed 25 to 50, Work-hardened 5 to 10
Tantalum <sup>d</sup>	Commercially pure	185 (27)	165 (24)	205 (30)	40
Co-Cr-Mo alloy (Elgiloy), heat treated at 525°C for 5 hours <sup>e</sup>	40Co, 20 Cr, 7Mo, 15.5Ni, 2Mn, 1Be, 0.15C, balance Fe	190 (28)	690 (100)	1020 (148)	>10
Gold <sup>d</sup> , annealed	≥99.99	79.9 (11.6)	nil	130 (19)	45
Gold <sup>d</sup> , 60% reduction	≥ 99.99	79.3 (11.5)	205 (30)	220 (32)	4
Platinum, annealed	99.95	164.6 <sup>f</sup> (23.9)	—	125 to 165 <sup>d</sup> (18 to 241)	30 to 40 <sup>d</sup>

[a] J.-M. Dorlot, J.-P. Bailon, J. Masounave, *Des Matériaux*, 2e édition, Éditions de l'École Polytechnique que Montréal, Montréal, 1986, 467 pages.

[b] www.matweb.com, as of 06/06/2003.

[c] Nitinol: <http://www.sma-inc.com/NITIProperties.html>, as of 06/06/2003.

[d] ASM International Handbook Committee, *Metals Handbook*, tenth edition, Volume 2: Properties and Selection: Nonferrous Alloys and Special-Purpose Materials, ASM International, Materials Park, Ohio, 1990, 1328 pages.

[e] ASM International Handbook Committee, *Nickel, Cobalt and Their Alloys*, ASM International, Materials Park, Ohio, 2000, 442 pages.

[f] J. Merker and D. Lupton, *Platinum Metals Rev.*, 2001, 45, 74.

effects could be observed in the body, even away from the implantation site.

### Leaching ions

Leaching, or releasing of metal ions, from surgical 316L stainless steel has also been investigated. It is well known that corrosion occurs to a significant degree in stainless steel implants, as it is susceptible to localized attacks in long-term applications. Nickel in the alloy can be extremely toxic in some forms, such as nickel carbonyls. Likewise chromium, also present in stainless steel, has been shown to release corrosion compounds that accumulate in tissues and red blood cells. Even if the released amounts of potentially toxic elements were very small, their long-term potential risk would have to be unequivocally evaluated prior to implantation. Because metallic stents are permanently implanted, it is very important that materials be safe on a long-term basis (at least as long as the rest of the life of the patient).

Another very interesting point about corroding materials is that corrosion is in fact an electrochemical reaction, which implies the presence of both a cathode and anode. In other words, when a metal (the anode) corrodes, a balancing reaction should take place at a cathode, causing chemical changes in the medium. Even if the metal is not corroding, anodic reactions can take place at its surface, implying a cathodic reaction somewhere else in the body.

Electrochemical tests have been carried out to investigate the relationship between biocompatibility and electrochemical behavior. It was found that the most biocompatible metals are those that

form semiconductive or nonconductive oxides at their surface, preventing redox reactions between the metal and the tissues. These metals include tantalum, niobium, and titanium.

### Surface properties

Surface properties are essential to stent performance. They include electrical surface charge, surface texture, and surface cleanliness.

- **Electrical charge:** Because platelets and plasma proteins are negatively charged, they should be attracted to metals that have a positively charged surface. Surprisingly, it appears from an *in vivo* study that no relationship exists between the attraction of these cells to the stent and its surface charge. The same study suggested that a higher surface charge leads to a low likelihood of hyperplasia (uncontrolled tissue proliferation).

- **Texture:** Surface texture is also important. *In vitro* tests made on flat and grooved Nitinol surfaces demonstrated that linear migration speed, alignment, and elongation of cells on the surface increase as a function of groove size (ranging from 1 to 22 microns). A grooved surface could thus enhance beneficial stent tissue ingrowth, which is always expected but rarely observed. On the other hand, because surface roughness increases specific surface areas exposed to the medium, texturing surfaces could increase the metal corrosion rate.

- **Cleanliness:** The cleanliness of stents is also an important factor. A substantial amount of foreign material has been found on handled stents, and also on untouched stents. These impurities, of unknown source, have been associated with stent-induced inflammatory response and stent failure. However,

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inflammatory response was lower when stents were rinsed under a high-pressure air jet just before implantation. Manufacturers and physicians should be aware of the danger of stent contamination and try to minimize it by developing appropriate industrial methods and fabrication routines.

### Mechanical properties

In the last decade, several studies have been carried out to improve the mechanical properties of stents. However, the function and the properties of the materials themselves have rarely been investigated. Suitable properties for a stent include easy trackability, ease of delivery, excellent radial strength, and a low recoil. The table presents the mechanical properties of the materials currently used for stent fabrication. Along with design, these properties will affect the trackability, ease of delivery, and radial strength of the stents.

- **Radial strength:** Radial strength is a very important property because the functionality of the stent, that is the ability to support the artery wall, is directly related. This is accepted as the main reason for which balloon-expandable stents are considered superior to self-expanding. When a force is applied to Nitinol, for example, the alloy assumes its martensitic (deformable) phase, and when the force is released, the alloy become austenitic (non-deformable). The high degree of deformability of martensitic Nitinol is believed to be responsible for the high acute recoil occurrence observed in the comparative study of several models of stents.

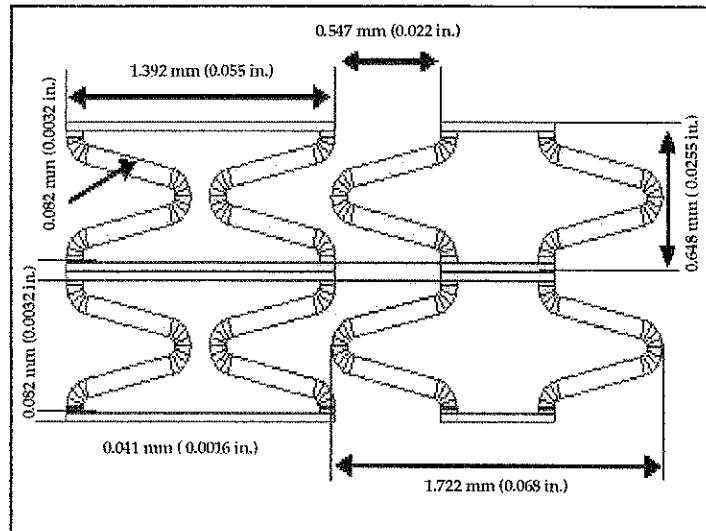
- **Elastic modulus:** Radial strength of balloon-expandable stents is also a function of the elastic modulus of the material after implantation, and of the design of the stent. The elastic modulus is an indication of the rigidity of the material.

From a theoretical point of view, two stents made of different materials with similar elastic moduli should show similar radial strength. However, with the first generation of coil stents this was not the case. In fact, their implantation was often associated with several clinical complications even when similar materials were used to fabricate the stents. Moreover, clinical procedures had not yet been fully developed. This underlines the importance of the design of the stent, its structure, and its mechanical properties.

- **Design:** Finally, it has been observed that appropriate design enables a very elastic structure even with a very rigid material. Moreover, materials that are more rigid allow the fabrication of stents with a smaller artery coverage. This is ideal for clinical applications in which small and short side-branch arteries have to be stented.

### Conclusion and future strategies

Stainless steel is the most common material for stent fabrication. Its physical properties are satisfactory, but not optimal. Stainless steel produces significant artifacts during magnetic resonance imaging (MRI), and its radiopacity is fair. However, tantalum exhibits excellent radiopacity and it is also MRI-compatible.



Geometry of a stent fabricated from a slotted hollow tube. The principal advantage of stents is that they may be implanted directly through the arteries, and do not require open-heart surgery. Diagram courtesy Symbiotech Medical Inc.

From a mechanical properties point of view, the materials for stents should possess comparable Young's moduli. Thus, the differences observed until now with different stents depend mostly on their design. Stainless steel, Nitinol, tantalum, and Co-Cr alloys apparently all possess sufficient strength to withstand stresses applied to them within the arteries. However, tensile strength of gold and platinum are low, as are their elastic moduli. Therefore, a stent entirely made of gold and platinum would exhibit poor radial strength.

Stents continue to be the source of many questions among researchers and physicians. Their long-term potential secondary effects are still unknown, and are unpredictable. It is the first time in history that metallic materials containing potentially highly toxic elements and compounds have been implanted directly in the heart, in contact with high-rate circulating blood. Furthermore, these materials are also submitted, during their implantation, to high deformations that generate significant stresses and phase changes.

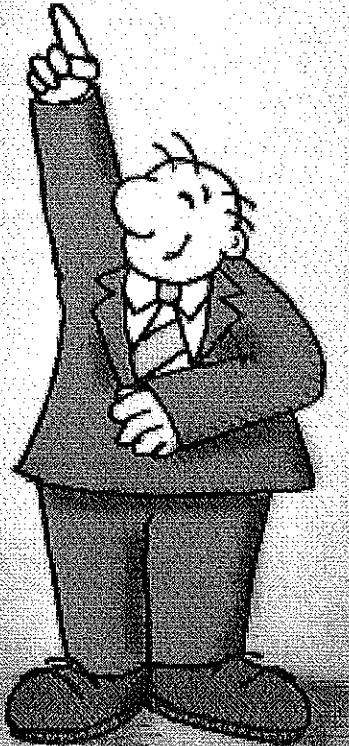
### New concepts in materials

The "perfect" stent does not exist, and it will probably never exist. However, several approaches have been or are currently under investigation to increase their clinical performance. One of these is the implanting of biodegradable stents made of nontoxic materials, either polymeric or metallic. The major clinical complication with stents is restenosis, defined as the blockage of blood flow by the coagulation of blood inside the stent. Because restenosis occurs within six months of implantation, biodegradable stents that are able to support the artery wall during this period of time may overcome problems related to the permanent nature and the potential long-term toxicity of metallic coronary stents available commercially today.

A new concept of degradable metal has been

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## Carcinogenicity of various metallic compounds

Trace element symbol	Element or compound	Evaluation
Be	Beryllium and its compounds	1
Cd	Cadmium and its compounds	1
Cr	Hexavalent chromium compounds	1
Cr	Trivalent chromium compounds	3
Cr	Metallic chromium	3
Co	Cobalt and its compounds	2B
Ni	Nickel compounds	1
Ni	Metallic nickel	2B

1: carcinogenic in humans. 2: possibly carcinogenic in humans. 3: non-classifiable as carcinogenic in humans. Metals classified according to their carcinogenicity as established by the U.S. International Agency for Research on Cancer.

proposed for stent fabrication, by considering magnesium-base alloys. In fact, magnesium alloys are well recognized for their high degradation rate, and magnesium stents may also address the clinical need to increase

the daily intake of magnesium in the general population, by releasing magnesium into the body as they degrade

Drug-coated stents are also under investigation and development.

Polymers could be used to coat metals, or to manufacture degradable or permanent stents. Encouraging results have already been seen with polymer-based Poly-L-Lactic Acid (PLLA) coronary stents. However, one of the major drawbacks of polymers is their lack of radiopacity and weak mechanical properties.

To improve stent blood compatibility, seeding stents with endothelial cells has also been investigated, with limited success. Different metallic materials or metallic and ceramic coatings have also been studied, in order to decrease their leakage of potentially toxic compounds and therefore improve their long-term safety.

Finally, it appears evident from this work that the potential and the need for materials with targeted properties is extremely urgent in the field of coronary stents. In the coming years, as biology and material sciences evolve, we will most certainly witness a true revolution in medicine.

Challenging new concepts have only begun in the field of endovascular surgery, and minimally invasive surgery (laparoscopy) is now being combined with magnetic resonance imaging to push the science beyond the existing medical frontiers. New

horizons must be opened, and clinicians, materials scientists, and manufacturers must quickly and truly work in close collaboration, as mastering such complex problems necessarily requires a multidisciplinary approach.

*The "perfect" stent does not exist, and it will probably never exist.*

As a result, numerous applications have been considered and many more are or will be envisaged.

This is undoubtedly the perspective by which the development of "functional materials," which have targeted surface and volume properties, must be regarded and analyzed. However, as we deepen our knowledge, our evaluations must become more rigorous. We must learn from past experience and adopt a rational approach if we are to face and overcome tomorrow's technological challenges without compromising the future health and welfare of patients and society. ■

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12-m

## Metal Stations

1. **Cost of a Penny** - directions on handout in notebook - page 14-M. Make sure that you see silver-colored zinc exposed on the post-82 pennies after sanding.
2. **Brassing a Penny** - Alloying Copper and Zinc - Battelle Manual page 5.7 and handout in notebook - page 17-M. Use a hot plate for the final brassing step instead of a torch or burner.
3. **Rolling a Penny** - directions and observation sheets in notebook - page 26-M.  
Try rolling both an old and a new penny.  
Observe differences under a microscope.  
Notice changes due to work-hardening.  
There are observation and math interpretation sheets in your notebook.
4. **Drawing Wire** - directions and observation sheets in notebook - page 30-M.  
Also found in the Battelle Manual on page 5.16  
There are observation and math interpretation sheets in your notebook.
5. **Lead/Tin Solder Lab** - follow the directions below. Written up in the Battelle Manual page 5.10. Notes also found in notebook - page 34-M. Bismuth may be substituted for the lead.
  1. Choose one of the labeled Dixie cups. Make 50 grams total of the given alloy.
  2. Mass out the correct amount of tin and lead (or bismuth).
  3. Melt the metals together in an evaporating dish using a hot plate.
  4. Mix with a glass stirring rod and gently scrape the oxidation to the side.
  5. Using pliers pour the molten metal into one depression in the spot plate - try to make it level with the surface of the spot plate. **CAUTION:** Make sure the spot plate is absolutely dry!!!!
  6. Pour the remaining metal into the sinker mold.
  7. Quench the metal pieces in a can of water.
  8. Put the spot back in the labeled Dixie cup and give to an instructor. You may keep the sinkers.
6. **Melt Tin and Pour into Hot and Cold Molds or Drip onto Different Surfaces**
  - a. Compare the freezing rates.
  - b. Compare size of crystal grains.
  - c. Bend to failure after cooling.

# THE COST OF A PENNY

## Day #1

1. Make a table to record your data. Record the date of a pre-1982 penny and a post-1982 penny.
2. Measure and record the thickness (using the digital calipers) and the mass (centigram balance) for each penny.
3. Use sandpaper to remove a thin layer around the rim of the penny - make sure that you see silver-colored zinc exposed on the post-82 pennies. Or use a triangular file to make four 1mm deep scores in the penny's edge at 90 degrees apart.
4. Place the pennies in a beaker or plastic (PS) cup and add 20 - 25 mL of 6M HCl.
5. Place in the fume hood or by an open window.
6. Write observations.

## Day #2

1. Decant the HCl into the sink, flushing with plenty of water. Add about 50 mL of tap water to the beaker to rinse off the pennies. Pour the water off and tip the pennies onto a paper towel to dry.
2. Measure and record the thickness and mass of each penny. Write observations about changes in appearance of each penny.
3. Answer the "Questions and Calculations" on the handout.
4. Write a final summary paragraph and a reflection paragraph.

## Safety

Safety glasses/goggles must be worn during this experiment.

The beaker containing the 6M HCL should be placed in a fume hood or by an open window overnight.

## Questions and Calculations:

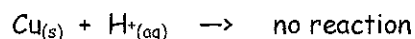
Record in your journal and show your work:

1. From the masses of the new penny before and after the reaction, calculate the mass of zinc in the new penny. Also determine the mass of copper in the new penny.
2. Calculate the percentage of zinc and the percentage of copper in the new penny.
3. From a newspaper look up the prices of copper and zinc at the present time. Note the units. If the units are in cents per pound, convert the value to cents per gram.  
(1 pound = 454 grams)
4. From the mass of zinc and the current market value of zinc, calculate the value of zinc in the new penny. Do the same for the copper in the new penny.
5. Determine the value of the copper in the pre-1982 penny.
6. Why do you think our government switched to a copper-clad zinc penny?
7. Zinc is approximately twice as expensive as lead. Hypothesize why don't we use lead in the center of our pennies instead of zinc?
8. Explain what happened to the new penny when placed in the HCl in terms of oxidation/reduction and the relative activity of copper and zinc.

## Notes:

1982 pennies are not used in this lab because that was the transition year for making the copper-clad zinc penny. Some 1982 pennies have a zinc core and others are copper. At the conclusion of the lab, students should be able to suggest a way to determine whether a 1982 penny is all copper or has a zinc core. The all copper pennies have a higher mass because copper is more dense than zinc. By massing a 1982 penny on a balance, students should be able to predict which type of penny it is. All copper pennies have a mass of approximately 3.2 grams and the "new" pennies have a mass of approximately 2.5 grams.

This lab works because of the different reactivities of copper and zinc to hydrochloric acid. Copper is below hydrogen on the activity scale and zinc is above hydrogen. Thus, when placed in HCl, the copper does not react and remains unchanged (removal of oxidation may cause a change in appearance of the penny). Zinc will react and replace hydrogen and enter the solution as a positive ion (it is **oxidized**). Hydrogen gas bubbles will be visible as the positive hydrogen ions are **reduced** to hydrogen atoms ( $H_2$  molecules). This is an example of both a single replacement reaction and an oxidation-reduction reaction.



The scores must be adequately wide to ensure enough surface area for all of the zinc to react and go into solution. Sometimes a penny will have solid zinc left in the core the second day. It is possible to carefully open the copper "shell" so that the rest of the zinc will react. Using sandpaper around the rim instead of making notches with a file increases the chances of all of the zinc reacting and the 2 halves of the penny coming apart. On occasion, the pennies will float and "dance" as hydrogen gas builds up inside the copper shell and then will sink when they "burp" the bubbles loose.

Possible assessment questions could include the following:

1. Someone hands you a penny minted during the year of transition (both solid copper and copper-clad zinc pennies were made that year). Describe a method you could use to determine if the penny was solid copper or copper-clad zinc. Include sample data or evidence that would support your claim.
2. Rank the following elements in order of reactivity. Conclude how this caused the results of the "cost of a penny" lab.

copper, hydrogen, zinc

16-m



## Brassing a Penny (Alloying Copper and Zinc)

Wear safety glasses and aprons!!!!

Journal observations throughout the procedure in your notebook.

### Method:

1. Obtain 3 pennies.
2. Clean the pennies thoroughly of all oxidation using Tarnex and/or steel wool. You might want to wear plastic gloves when using Tarnex. Wash with soap and water and thoroughly dry. Do **NOT** touch the pennies with your skin after washing them. Oil from your skin can keep the zinc from plating properly.
3. Set one penny aside for comparison.
4. Go to the zinc-plating station. In the glass dish is a mixture of 1M NaOH and zinc dust. A zinc metal strip is submerged beneath the mixture and extends over the outside edge of the dish. Connect the DC voltage source (AA battery) by placing the positive alligator clip (red wire) on the zinc strip. You will use the negative alligator clip (black wire) on the copper tweezers.
5. Hold one of the pennies with copper wire "tweezers". Submerge the penny in the 1M sodium hydroxide solution containing zinc dust. Do not touch the penny to the zinc dust on the bottom of the dish. Touch the negative alligator clip to the copper tweezers for a few seconds (start with about 8 seconds). Remove the alligator clip from the tweezers and then check the plating. Repeat as necessary to get full coverage. Quickly rinse the penny in a cup or beaker of distilled water.
6. Repeat step 5 with a second penny.
7. Rinse the zinc-plated pennies under running water. Dry the pennies.
8. **Caution:** Do not use paper towels to remove zinc dust and/or sodium hydroxide solution from the pennies. A combination of paper, zinc dust, and sodium hydroxide can cause a fire. Rinse in water.
9. Set one penny aside for comparison.
10. Place the remaining penny on a warm hot plate. When a color change occurs, push the penny into a beaker of distilled water. Dry.
11. Clean up everything!!!!

**Summary/Conclusions:** Answer the following questions in your journal.

1. Describe the differences in the appearance of the 3 different pennies. What metal is on the surface of each?
2. How was the brass formed - physically or chemically? Support your answer.
3. Explain what happened to the copper and zinc atoms in the formation of the brass.
4. Is brass a compound or a mixture?
5. Define alloy.
6. Discuss the purposes of alloying.

**Note about student misconceptions:**

At first, I was surprised by the answers to question #2. Most students got it wrong. They interpreted the change in color due to heating as a chemical change. I can understand why they think this is so. After all, a color change is an indication of a chemical reaction. Heat is often a catalyst for a chemical reaction. Thus, in their eyes, the formation of the brass was a chemical change. This led to a productive discussion and review. We had previously discussed the four types of bonding: metallic, ionic, covalent, and intermolecular. Only two of these, ionic and covalent, produce a chemical change. They needed to be walked through the reasoning and reminded of what we had learned earlier. Since zinc and copper are both metals, ionic or covalent bonding does not occur. Metallic bonding is happening. Diffusion is a physical intermingling of atoms. Thus, brass is a solid solution and forming solutions is a physical process. It was neat to see the "light bulbs" go on.

## Teacher Notes:

Set-up for zinc-plating using cold solution:

- Small beaker or dish
- Zinc strip - bent to lay flat on bottom of dish/beaker, run up the side, and hang over and down the outside
- 1 M NaOH - deep enough to submerge a penny vertically and not have the penny touch the zinc dust on the bottom of the dish
- Zinc dust - cover the bottom of the dish

## Hints:

- It seems to work best if you submerge the penny in the solution and then touch the black wire to the copper tweezers.
- Also, it works best if you break the "circuit" before bringing the penny out of the solution.
- In other words, the penny shouldn't be connected to the battery unless it is submerged in the NaOH/zinc dust solution.
- A quick decision needs to be made as to whether enough plating has been done. The "wet" penny needs to either go back into the NaOH solution for more plating or into a cup/beaker of distilled water quickly and not be exposed to air for any length of time with the NaOH still on it.
- Use fairly thick gauge copper wire for the tweezers. Just bend it in half - a "curved" bend - and then use the "points" to pick up the penny. It doesn't have to be a "tight" grasp because the rims of the penny will prevent the tweezers from sliding off.
- It is crucial that all oxidation be removed from the pennies prior to the zinc-plating.
- A product called Tarnex works great for removing oxidation. It can be purchased at local stores.
- Also, have students avoid handling the pennies after cleaning them. Oil from their fingers can leave a coating on the pennies that interferes with the plating.
- It is also crucial that all Zn dust and NaOH solution be thoroughly removed/washed from the pennies after the Zn-plating process. This should be done under running water. Any residue wiped off and left on paper towels can create a combustion reaction and cause a fire.

## Alternative Method:

This lab can also be done using 1M  $\text{ZnCl}_2$  (zinc chloride - 135 grams per 1000 mL of solution) for the zinc plating. But the solution must be heated on a hot plate instead of using a battery. It needs to be kept hot but try not to let it boil continuously. Use about 25 mL of solution per 250 mL beaker and cover the bottom with zinc. Granular zinc can be used instead of zinc dust. Either one works, but the dust produces better results. Metallic dusts are a flammable hazard so caution is warranted. Place the cleaned pennies on top of the granular zinc in the hot zinc chloride solution. Once the pennies have changed color, turn them over with forceps. After the entire surface has changed color, let them sit for about another minute. Then rinse them in the distilled water and continue with the rest of the method listed on the first page.

## "The Buck Starts Here"

Science News, Vol. 157

April 1, 2000

Pages 216-217

1. Why did the U.S. Mint need to develop a new alloy for the golden dollar?
2. What 3 properties does a vending machine use to identify a coin?
3. Describe the composition of the golden dollar. Include the core and the alloy cladding.
4. What is the purpose of adding nickel to the alloy?
5. Pose a question that you would like to ask the author.

## The Buck Starts Here

### The U.S. Mint performed some neat tricks to make a golden dollar

By CORINNA WU

Poor Susan B. Anthony. A pioneering 19th-century advocate of women's rights, she suffered the misfortune of having her stalwart visage stamped on a wildly unpopular U.S. coin. Because the Susan B. Anthony dollar looks confusingly like a quarter, it never won the public's acceptance.

Now, 21 years after its introduction, the Susan B. Anthony is about to retire. On Jan. 27, the United States Mint shipped new golden dollar coins simultaneously to Federal Reserve Banks and the discount megastore Wal-Mart. Last month, the mint began an advertising campaign to introduce the coin to the public.

The new dollar is different from the Susan B. Anthony, inside and out. No stern mugshot adorns this coin. Instead, the luminous face of Sacagawea, the young Shoshone woman who guided the Lewis and Clark expedition from 1804 to 1806, gazes from the coin's face. She carries her sleeping infant son, Jean Baptiste, on her back. Its unique color and other features distinguish this coin from the Susan B. Anthony and the quarter.

The choice of metals used in the golden dollar took as much, if not more, work than the design did. "We pulled off a trick, a really nifty trick, when we chose the alloy for this coin," said Philip N. Diehl, the director of the U.S. Mint, addressing the National Press Club in Washington, D.C., on Feb. 23. That trick saved companies from the expensive task of retooling millions of vending machines and coin-operated devices around the country.

So far, it seems that the lessons learned from the Susan B. Anthony fiasco have paid off. The mint expects that within the first 3 months of release, demand for the Sacagawea dollar will reach more than half a billion coins, says Diehl. It took the Susan B. Anthony 14 years to reach that demand. The mint "cannot be satisfied with proving that the golden dollar is a beautiful racehorse," he adds. "Our goal is for it to become the workhorse of American coinage."

Even though consumers deemed the Susan B. Anthony a dismal failure, it's actually the most successful dollar coin the country has ever had. Nine hundred million are in circulation. The United States minted silver dollars sporadically between 1794 and 1935 and copper-nickel dollars bearing the image of Dwight D. Eisenhower from 1971 to 1978. In 1978, Congress authorized the minting of the Susan B. Anthony.

Why does the country need a dollar coin? For the mint, it's a good investment. The Sacagawea dollar coin, which costs 12 cents to make, can

The make-up of some U.S. coins

Coin	Penny	Nickel	Dime	Quarter	Half Dollar	SBA Dollar	Golden Dollar
<b>Obverse Design</b>	Abraham Lincoln	Thomas Jefferson	Franklin Roosevelt	George Washington	John F. Kennedy	Susan B. Anthony	Sacagawea
<b>Reverse Design</b>	Lincoln Memorial	Monticello	Torch, Olive Branch, Oak Branch	Eagle or State-Specific Designs	Presidential Coat of Arms	Apollo 11 Insignia, Eagle	Eagle
<b>Metal Composition</b>	Copper-Plated Zinc (97.5% zinc, 2.5% copper)	Copper-Nickel Alloy (75% copper, 25% nickel)	Copper-Nickel Clad* (91.67% copper, 8.33% nickel)	Copper-Nickel Clad* (91.67% copper, 8.33% nickel)	Copper-Nickel Clad* (91.67% copper, 8.33% nickel)	Copper-Nickel Clad* (87.5% copper, 12.5% nickel)	Manganese Brass Clad** (88.5% copper, 6.0% zinc, 3.5% manganese, 2.0% nickel)
<b>Weight (grams)</b>	2.5	5.0	2.268	5.67	11.34	8.1	8.1
<b>Diameter (millimeters)</b>	19.05	21.21	17.91	24.26	30.61	26.5	26.5
<b>Thickness (millimeters)</b>	1.55	1.95	1.35	1.75	2.15	2.0	2.0
<b>Edge Texture (Number of Ridges)</b>	Smooth	Smooth	Ridged (118)	Ridged (119)	Ridged (150)	Ridged (133)	Smooth

\*A pure copper core sandwiched between two layers of a 75 percent copper and 25 percent nickel alloy.

\*\*A pure copper core sandwiched between two layers of manganese brass, which consists of 77 percent copper, 12 percent zinc, 7 percent manganese, and 4 percent nickel.

21-m

last 30 years. A dollar bill, costing 3.5 cents, heads for the shredder after about 18 months. A popular dollar coin could earn a hefty profit for the U.S. Treasury, just as a successful product does for a private company.

Coins also work a lot better than bills in vending machines. "Paper money is fickle," says Thomas E. McMahon, vice president and counsel for the National Automatic Merchandising Association in Chicago. "Too many times, it's not read properly, which results in a lost sale or at least a frustrated customer." Also, machines give coins as change more easily than bills.

The escalating price of vending machine items and the dwindling supply of Susan B. Anthony dollars minted in 1979 and 1980 prompted Congress to enact legislation authorizing a successor. The United States Dollar Coin Act of 1997 specified that the new dollar coin be golden in color, have a distinctive edge, and be the same size as the Susan B. Anthony. In other words, the coin has to look and feel different to consumers but resemble the Susan B. Anthony closely enough to fool vending machines.

Importantly, the act did not eliminate the dollar bill. Legislation that would have done that "sat in Congress and went nowhere for about 15 years," Diehl says. The proposal to make a coin along with the current dollar bill "flew through Congress [and] landed on the president's desk within 4 or 5 months."

The Sacagawea coin has the same luster as 14-carat gold, though it does not actually contain the precious metal, says Michael White, a U.S. Mint spokesperson. It has a wider border than other coins do and a plain, smooth edge just like the nickel. It's 26.5 millimeters in diameter and weighs 8.1 grams, making it slightly larger than the quarter.

Testing done by the mint shows that consumers, both sighted and visually impaired, can pick out the coin by feel without trouble, says White.

Whereas the coin must be distinctive to people, the country's 15 million vending machines need to treat it the same as the Susan B. Anthony. Had businesses been obliged to retune all of their machines, says McMahon, many would have been unwilling to do so, which would in turn have hurt the coin's success.

A new alloy developed by Olin Brass in East Alton, Ill., which has supplied the U.S. Mint with materials since 1964, allowed Sacagawea to masquerade as Susan B. Anthony. Vending machines identify a coin by its weight, size, and so-called electromagnetic signature. Vending machines typically test a coin's electrical conductivity by passing an alternating current through it and measuring the induced magnetic field, says Dennis R. Brauer, Olin's vice president of technology.



U.S. Mint

The coin shows Sacagawea carrying her son. Some people have questioned the accuracy of the portrayal, noting that the Shoshone carried their infants on cradleboards facing backwards. Historians and other experts consulted by the U.S. Mint have said that at times during the journey, Sacagawea probably did carry Jean Baptiste in a sling. Lucky for the mint; the design is more aesthetically pleasing if the baby faces forward.



U.S. Mint

The reverse side of the golden dollar coin depicts an eagle—required by the United States Dollar Coin Act of 1997—surrounded by 17 stars, one for each state in the Union at the time of the 1804 Lewis and Clark expedition.

Metallurgists at the mint could match the Susan B. Anthony's size and weight easily, but duplicating its electromagnetic properties proved to be much trickier. That signature depends on both the type of metal and the construction of the coin.

Like all silver-colored U.S. coins, the Susan B. Anthony consists of a pure copper core sandwiched by two layers of a copper-nickel alloy. The material is durable, easy to stamp with a design, and tarnish-resistant. To make test coins, the mint asked Olin Brass to provide about 25 alloys in different thicknesses—a total of more than 30,000 samples. They hoped to find a coin that would duplicate the Susan B. Anthony's electromagnetic signature.

Nothing worked. "All the golden color alloys had three times too much conductivity," Brauer says.

What's more, different companies use different frequencies of alternating current in their coin acceptors, compounding the problem. "The higher the frequency, the shallower the penetration into the coin," Brauer explains. "At higher frequencies, you measure only the surface conductivity. Lower frequencies penetrate into the core."

Metallurgists at the U.S. Mint tried many different combinations of alloys and coin constructions, trying to offset the higher conductivity with different metal-layer thicknesses. "They could easily match it for one machine, but it was not universal," Brauer notes.

Last May—3 months before manufacturing was to start—the mint was ready to concede and go with an alloy that did not satisfy the electromagnetic requirements. Researchers at Olin Brass, however, had a final brainstorm. They knew of some manganese alloys that have low conductivities, but these materials are pink, Brauer says. By adding enough manganese and zinc to copper, the researchers thought they might get a golden alloy with the right electromagnetic properties.

The strategy worked. After adding some nickel for tarnish resistance, they told the mint about the brand-new material. "I sent them five sample coins, then eventually a 40,000-pound lot, and the rest is history," says Brauer.

The final alloy consists of 77 percent copper, 12 percent zinc, 7 percent manganese, and 4 percent nickel. The pure copper core makes up half of the metal in the coin, with the two layers of manganese brass each taking up one-fourth of the thickness.

For coins, counterfeiting isn't a big problem—it's more profitable for a crook to print fake twenties and fifties. Vendors do worry, however, about unscrupulous customers feeding slugs, or fake coins, into their machines.

The sandwich design as well as the unique properties of the alloy make slugging difficult to carry off. Olin Brass casts the material in 10-ton ingots, then squeezes them between rollers to get them down to the proper thickness. "It's not something you can do in your garage," Brauer notes.

Because the new dollar costs only 12 cents to make, Diehl notes, the mint recovers a healthy 88-cent profit on every dollar coin it sells. The Sacagawea dollar will help the U.S. Mint continue to make a lot of money—in more ways than one.

In designing the coin, the U.S. Mint took the unprecedented step of soliciting comments from the public. More than 130,000 people sent their ideas via letters, faxes, and electronic messages. In June 1998, a design advisory committee that reviewed the input recommended that the dollar coin honor Sacagawea.

The mint then invited 23 artists to submit designs. After consulting representatives of the Native American community, historians, artists, educators, and the public, the mint chose sculptor Glenna Goodacre's design. For the eagle on the coin's reverse side, it chose a design by mint engraver Thomas D. Rogers Sr.

The Sacagawea design is "surprisingly effective," says John M. Kleeberg, curator of modern coins at the American Numismatic Society in New York. "So much of the stuff produced by the

U.S. Mint has been terrible. The modeling of Sacagawea is nicely done, and the pose is an unusual one. We don't know what she looked like, but [on the coin] she doesn't look like a cold goddess."

Coins with simple designs continue to look good even as they wear down, Kleeberg says. The new golden dollar follows that precept.

People seem to be taken with the Sacagawea dollar, Diehl says. "Banks and retailers that never indicated any interest in this coin and had never ordered a single Susan B. Anthony coin wanted it immediately because the American people wanted it. . . . It really is a stunningly beautiful product. . . . It connects with people, and they want to have and hold it."

People who want to pocket the new dollars can get them a variety of ways. The mint sells the coins on its Web site (<http://www.usmint.gov>), banks and Wal-Mart stores carry them, and a few lucky breakfast-cereal eaters might find them in boxes of Cheerios.

The U.S. Mint predicts that demand for the golden dollar will reach 1 billion coins by the end of the year, more than the Susan B. Anthony could muster in its entire lifetime.

And though there's no gold in the circulating dollar coin, collectors will be happy to know that the mint will start making a 22-carat-gold version this summer—for anyone who can come up with considerably more than a buck. □



## Composition of Alloys

In industry as well as in the lab, alloys are created by physically combining solids to make a mixture.

1. Jewelry and tableware are sometimes made of sterling silver. Sterling silver is 92.5% silver (Ag) and 7.5% copper (Cu). If you wanted to make 30 grams of sterling silver for a ring, how many grams of silver and copper would you need to start with?
2. Some gold used for jewelry is called '18-karat white gold'. This alloy is 75% gold (Au), 12.5% silver (Ag), and 12.5% copper (Cu). If you wanted to make 25 grams of 18-karat white gold for a ring, how many grams of each metal would you need to start with?
3. In jewelry, 14-karat gold is not pure gold. It is actually 58% gold (Au), 4 to 28% silver (Ag) and 14 to 28% copper (Cu). When you buy a 10 gram ring, how many grams of gold are you really getting?
4. Solder is used for electronic connections and for making stained glass projects. Electronic solder is specifically 63% tin (Sn) and 37% lead (Pb). To make 75 grams of solder, how many grams of each metal would you need to start with?
5. Bronze is typically used for statues and castings. If a sample of bronze was created using 85% copper (Cu), 10% zinc (Zn), and 5% tin (Sn), how many grams of each metal are required for a 150 gram statue?

## Rolling a Coin

### Method:

1. Use a caliper to measure the thickness of a penny. Record in cm.

Record date of penny.

Trace around penny on graph paper.

Count number of full squares. Record.

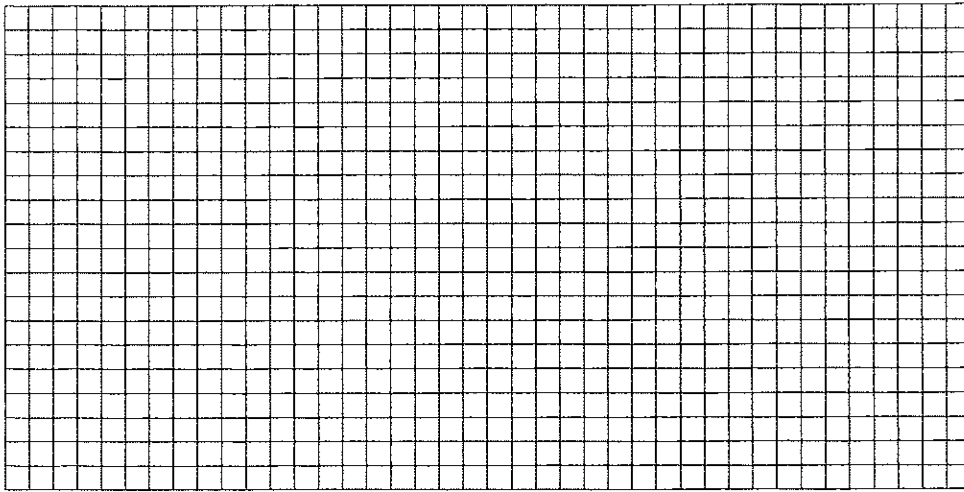
Count number of partial squares. Divide number of partial squares by two. Record.

Add this number to number of full squares to get approximate area.

2. Adjust the rollers on the rolling mill so the penny just fits snugly. Roll penny.
3. Adjust rollers no more than  $1/8$  of a turn and roll again. Flip the penny 180 degrees between each roll. Do NOT tighten too much or use an excessive amount of force.
4. Continue to gradually adjust rollers and roll penny. Record observations. **STOP** rolling **before** the penny out grows the graph paper!!!!!!!!!!!!
5. Determine new thickness and new area using the same procedure in Step #1. Record.
6. You may continue rolling after tracing new area as time allows. You may also want to try comparing a "new" (post-1982) and an "old" (pre-1982) penny.

## Rolling a Coin - Observations

1. Date on penny: \_\_\_\_\_
2. Thickness of penny: \_\_\_\_\_
3. Trace the unrolled penny on the graph.



Number of full squares: \_\_\_\_\_

Number of partial squares: \_\_\_\_\_  $\div 2 =$  \_\_\_\_\_

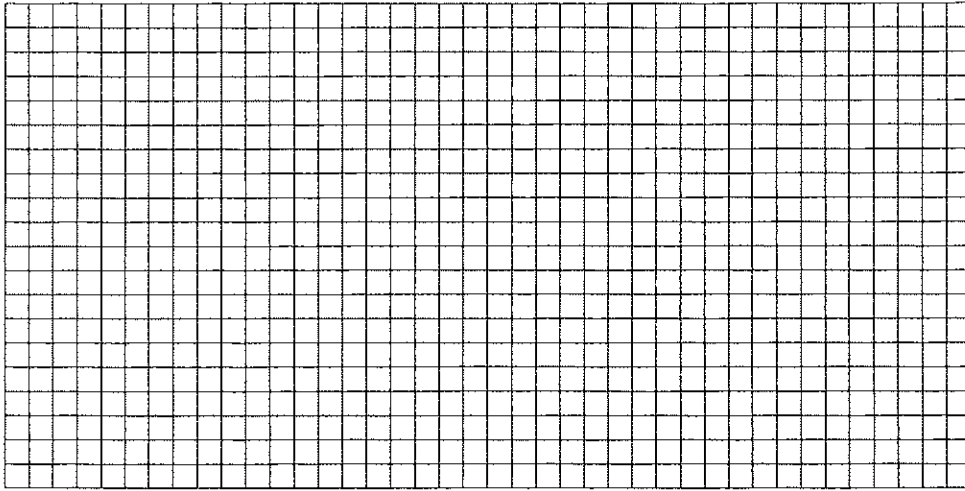
Penny's area = \_\_\_\_\_ squares

4. Thickness of the rolled penny: \_\_\_\_\_

Description of the rolled penny:

Composition of the penny:

5. Trace the rolled penny on the graph.



Number of full squares: \_\_\_\_\_

Number of partial squares: \_\_\_\_\_  $\div$  2 = \_\_\_\_\_

Penny's area = \_\_\_\_\_ squares

6. Additional observations and impressions:

## Rolling a Coin

### Math Interpretation Questions

1. The penny at the start was how many times as thick as it was after being rolled?  
Show your work.
  
2. After being rolled, the penny had an area \_\_\_\_\_ times as great as it did at the start. Show your work.
  
3. Calculate the volume of the penny at the start and after it was rolled. Compare the two volumes and explain the result. Show your work.

Volume = area  $\times$  thickness

## Drawing a Wire

### Method:

1. Cut approximately 15 cm of copper wire. Record actual length.  
  
Use a caliper to measure diameter in cm and record.  
  
Use a balance to measure mass in grams and record.
2. Clamp the drawplate into vise horizontally. Use paper towels to protect from jaws. The larger openings of the dies should be on the backside.
3. Taper the end of the wire with a file or the sander.
4. Pass wire through smallest hole that tapered end will go through. Use a lubricant on the wire. Record the number of the hole.
5. Use draw tongs to grasp wire and smoothly pull it through the die. Record observations.
6. Repeat this process through at least 10 holes. Record the number of the die that you last pull the wire through.
7. Measure and record final length, diameter, and mass.

### Hints: (otherwise known as frustration relievers)

Pull the wire through the same die twice before moving to the next smaller hole.

If the wire becomes too stiff and brittle, stop and heat treat it.

Keep a taper on the end.

Don't jerk - pull slowly and steadily.

Keep the wire lubricated.

## Drawing a Wire - Observations

1. Type of wire used: \_\_\_\_\_
2. Initial length: \_\_\_\_\_
3. Initial mass: \_\_\_\_\_
4. Initial diameter: \_\_\_\_\_
5. Size of hole in the die through which the wire was first drawn: \_\_\_\_\_
6. Make and fill in a data table to display the length and diameter of the wire after every three holes the wire is drawn through.

7. As the wire is being drawn through the die, what happens to the wire's

Length: \_\_\_\_\_

Diameter: \_\_\_\_\_

Temperature: \_\_\_\_\_

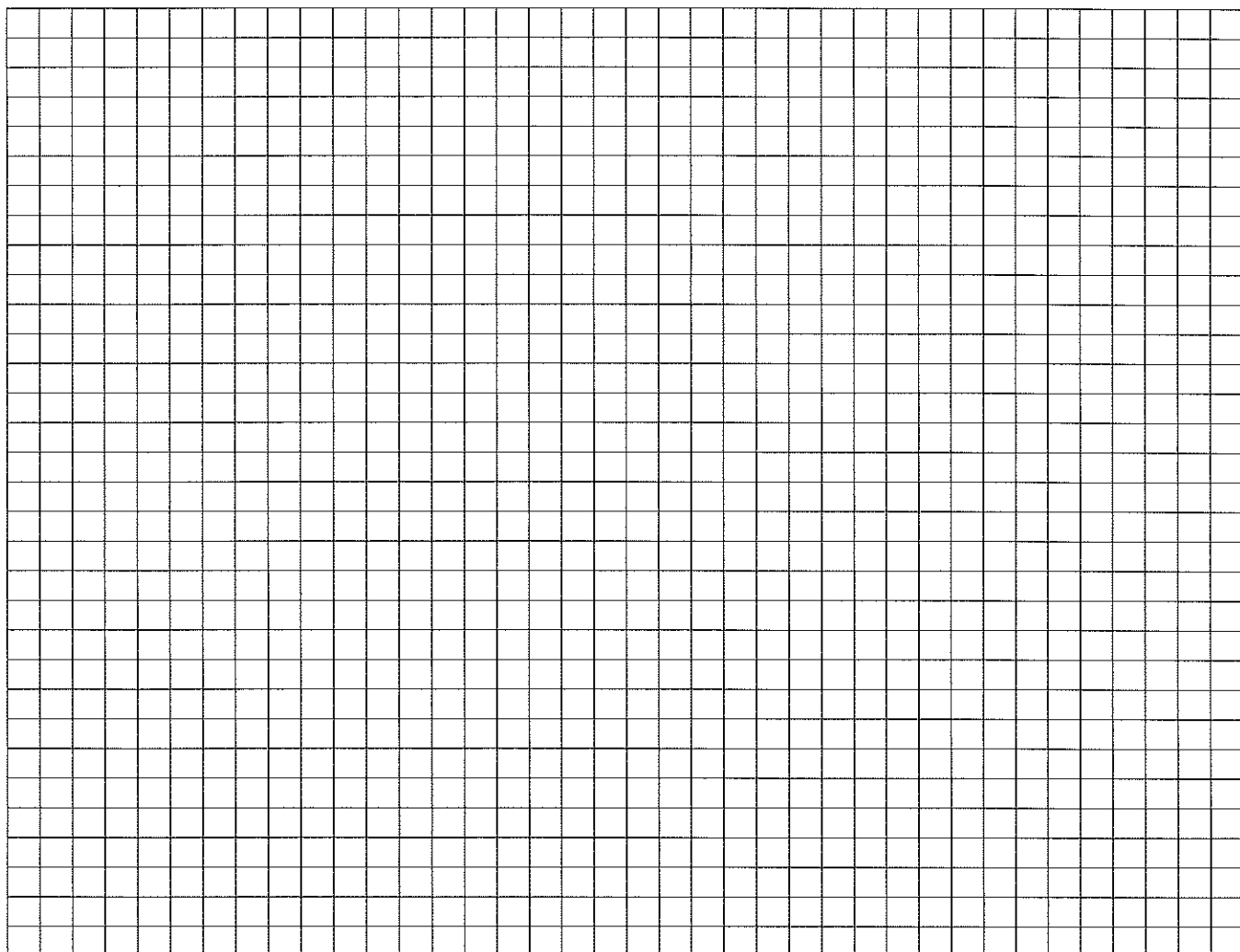
8. Size of hole in the die through which the wire was last drawn: \_\_\_\_\_

9. Final length: \_\_\_\_\_

10. Final mass: \_\_\_\_\_

11. Final Diameter: \_\_\_\_\_

12. Graph the data collected (length and diameter).



13. Additional observations and impressions:

32-m



## Drawing a Wire

### Math Interpretation Questions

1. Which dimension of the wire changed the most during the drawing process?  
mass, length, or diameter

Suggest a reason why that one changed more than the other two.

2. Hypothesize what you think happened to the density of the wire during the drawing process.

3. Calculate the wire's initial volume and final volume. Compare the two volumes and explain the result. Show your work.

$$\begin{aligned} \text{wire's volume} &= \text{radius} \times \text{radius} \times \text{pi} \times \text{length} \\ (V &= r^2\pi h) \end{aligned}$$

## Lead/Tin Solder Lab

1. Copy the table of assigned lead/tin percentages into your journal.
2. Mass out 50 grams total of your assigned lead and tin alloy.
3. Melt the metals together in an evaporating dish using a hot plate
4. Mix with a glass stirring rod and gently scrape the oxidation to the side. Hold the evaporating dish w/ needle-nose pliers.
5. Using pliers pour the molten metal into one depression in the spot plate - try to make it level w/ the surface of the spot plate. **CAUTION:** Make sure the spot plate is absolutely **dry!!!!!!!!!!!!**
6. Pour the remaining metal into the warm sinker mold.
7. Quench the metal pieces in a can of water.
8. Put the metal spot into a labeled plastic bag and give to the teacher. You may keep the sinkers.

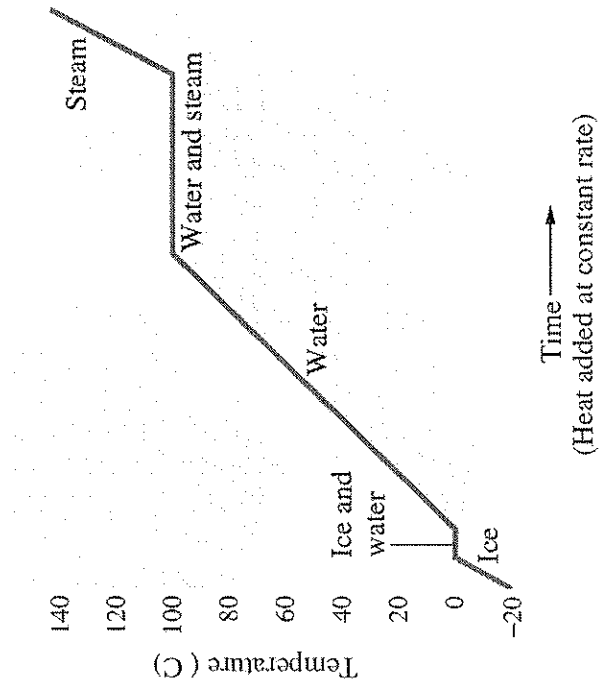
100% Pb 0% Sn	90% Pb 10% Sn	80% Pb 20% Sn	70% Pb 30% Sn	60% Pb 40% Sn	50% Pb 50% Sn	40% Pb 60% Sn	30% Pb 70% Sn	20% Pb 80% Sn	10% Pb 90% Sn	0% Pb 100% Sn

35-m

**-phase diagram for water**

- *Typical diagram for pure substances - elements and compounds - same typical shape - different temps*
- *Heating a solid, melting a liquid, boiling a liquid, heating a gas (vapor)*
- *Heat is changing the whole time, temperature does not increase during a phase change (change of state)*
- Heat - total energy, potential and kinetic
- Temperature - average kinetic energy

Figure 11.9: Heating curve for water.



Phase - material that has its own structure and/or composition

Phase change -

- Change in state
- Change in crystalline structure (*solid state phase change*)
- Energy is absorbed or released
- Temperature does not change
- *Particles held together more tightly - energy was released*
- *Particles less closely attracted - energy was absorbed*

-phase diagram for iron

- *Same as for water - "backwards" - shows a release of energy instead of an absorption in energy*
- *Has additional flat lines - phase changes that are not changes of state - represent solids state phase changes such as a change in crystalline structure*

-binary phase diagram for Pb/Sn solder

- *Plots percent composition versus temperature*
- *Pass out student copy*
- *Does not include gas state*
- Label the all liquid region
- Label the all solid region
- Label the liquidus line - only liquid above the line
- Label the solidus line - only solids below the line
- Ask what is between the 2 lines - slush zone
- Slush - combination of solid and liquid - amounts of each varies based on temperature and percentage composition - compare to a slurpee
- Eutectic - mixture composition that acts like a pure substance

37-3

- Eutectic composition - composition with the lowest melting temp
- Eutectic point - lowest melting temperature of the alloy - *temp at which eutectic composition freezes*

-The solidus line touches the liquidus line in 3 places - on the left edge of the graph and the right edge of the graph which are the melting points of the pure metals (elements) and the eutectic point.

-Pure substances have a melt point - a temperature at which it melts - no temp change until melting is completed

-Mixtures have a melt range - a temperature at which it starts melting and a higher temperature at which it completes melting

-melt an ice cube on the griddle - point out that it goes directly from solid to liquid, no slush.

-melt the solder spots on the griddle - gradually turning up the temperature (heat)

-compare the phase diagram to what they are seeing with the melting spots on the griddle

-have the students predict:

- Which spot will melt first
- Which spot should melt start melting second, etc...
- Which spots will have slush as they melt
- What will happen if you stop increasing the temperature while a spot is in the slush zone
- Which spot has the biggest slush range
- Which spots won't melt
- What will happen if you turn off the heat

After melting, resolidifying, and melting again, review the phase diagram.

Have students pick out the liquidus line, solidus line, and eutectic point on other sample binary phase diagrams.

**Websites:** Very useful for your own study and learning. Some are much more in depth.

<http://www.chemguide.co.uk/physical/phaseeqia/snrb.html>  
lead/tin solder and phase diagrams

[http://www.ae.utexas.edu/courses/ase324\\_huang/Lecture7.pdf](http://www.ae.utexas.edu/courses/ase324_huang/Lecture7.pdf)

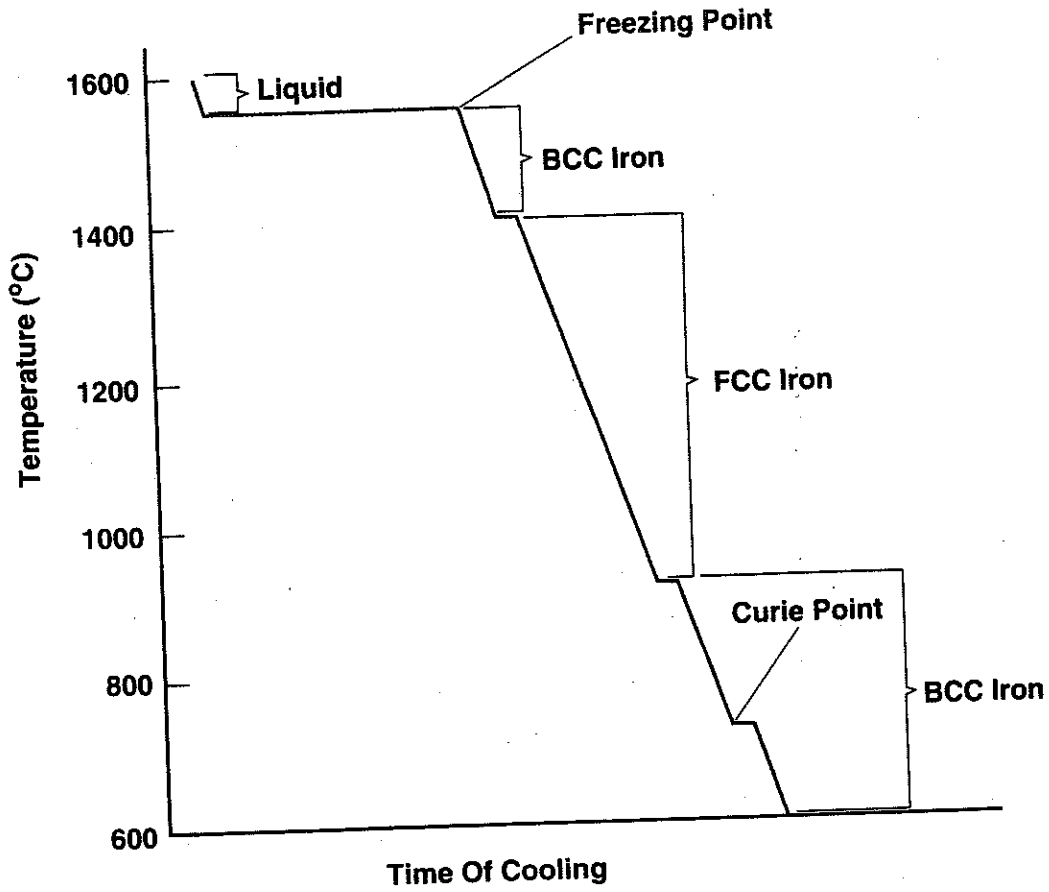
<http://www.soton.ac.uk/~pasr1/>  
tutorials and quizzes on phase diagrams - looks excellent

<http://people.virginia.edu/~lz2n/mse209/Chapter9c.pdf>  
phase diagrams and the lever rule

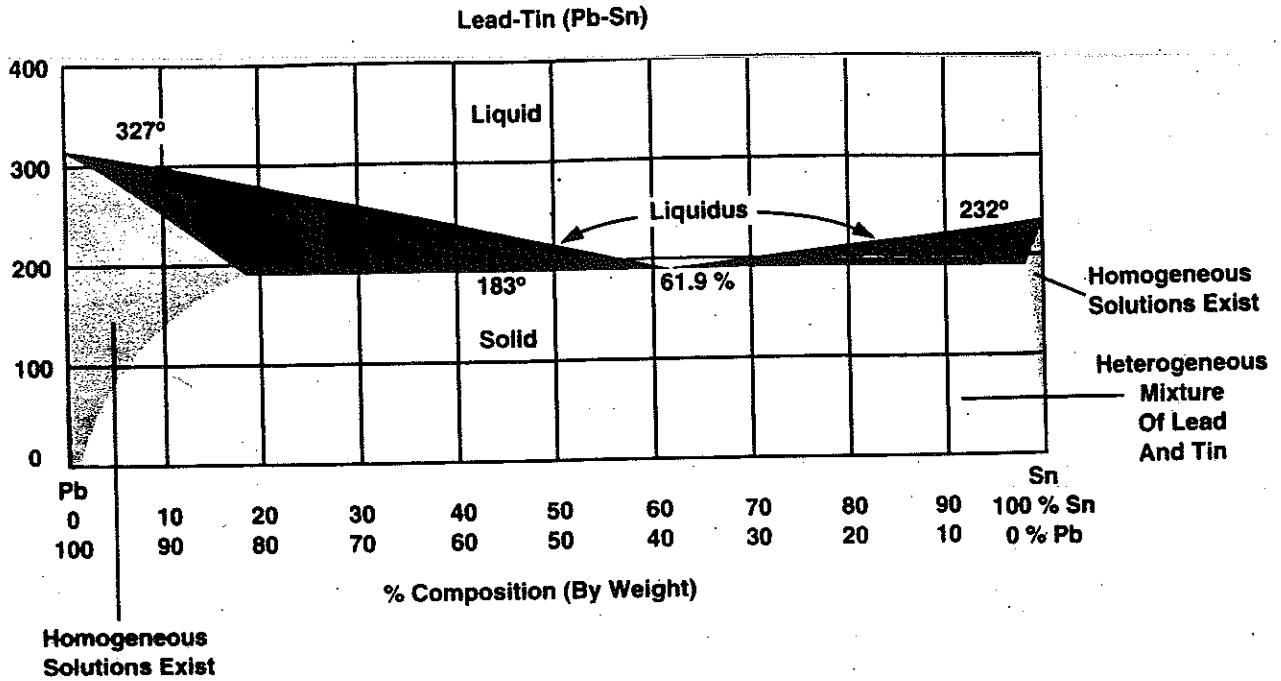
<http://www.doitpoms.ac.uk/tlplib/CD4/index.php>  
phase diagrams and solidification

<http://www.intute.ac.uk/sciences/cgi-bin/search.pl?term1=phase+diagrams&limit=0>  
list of websites about phase diagrams - lots of good ones

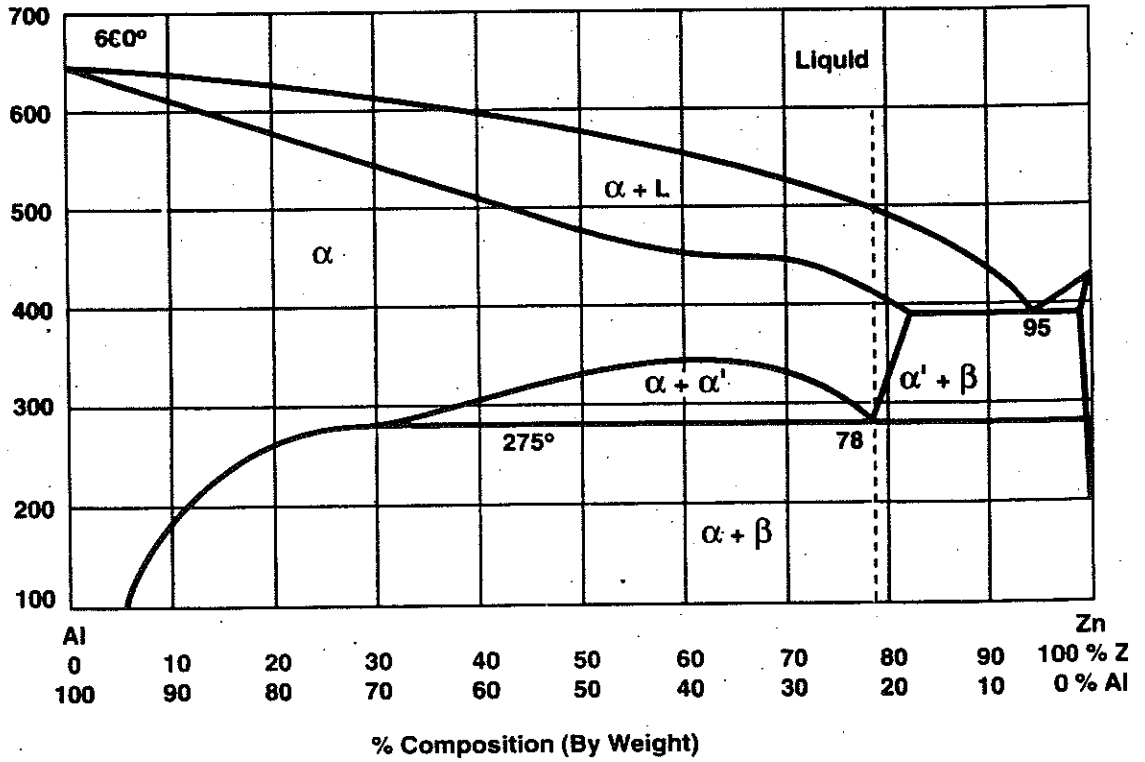
# Phase Diagram of the Cooling of Iron





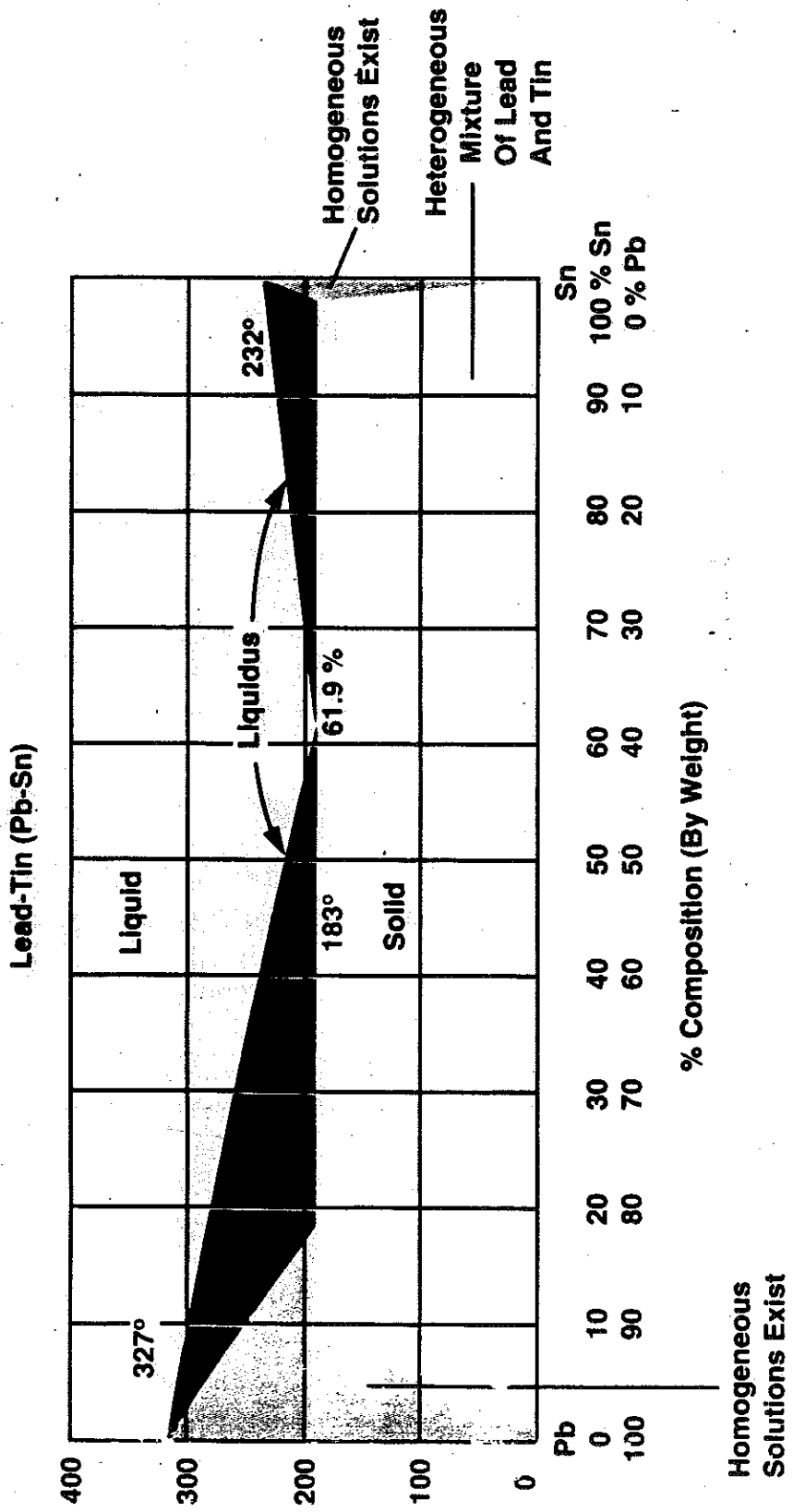


**Figure 11**  
A binary phase diagram for lead and tin



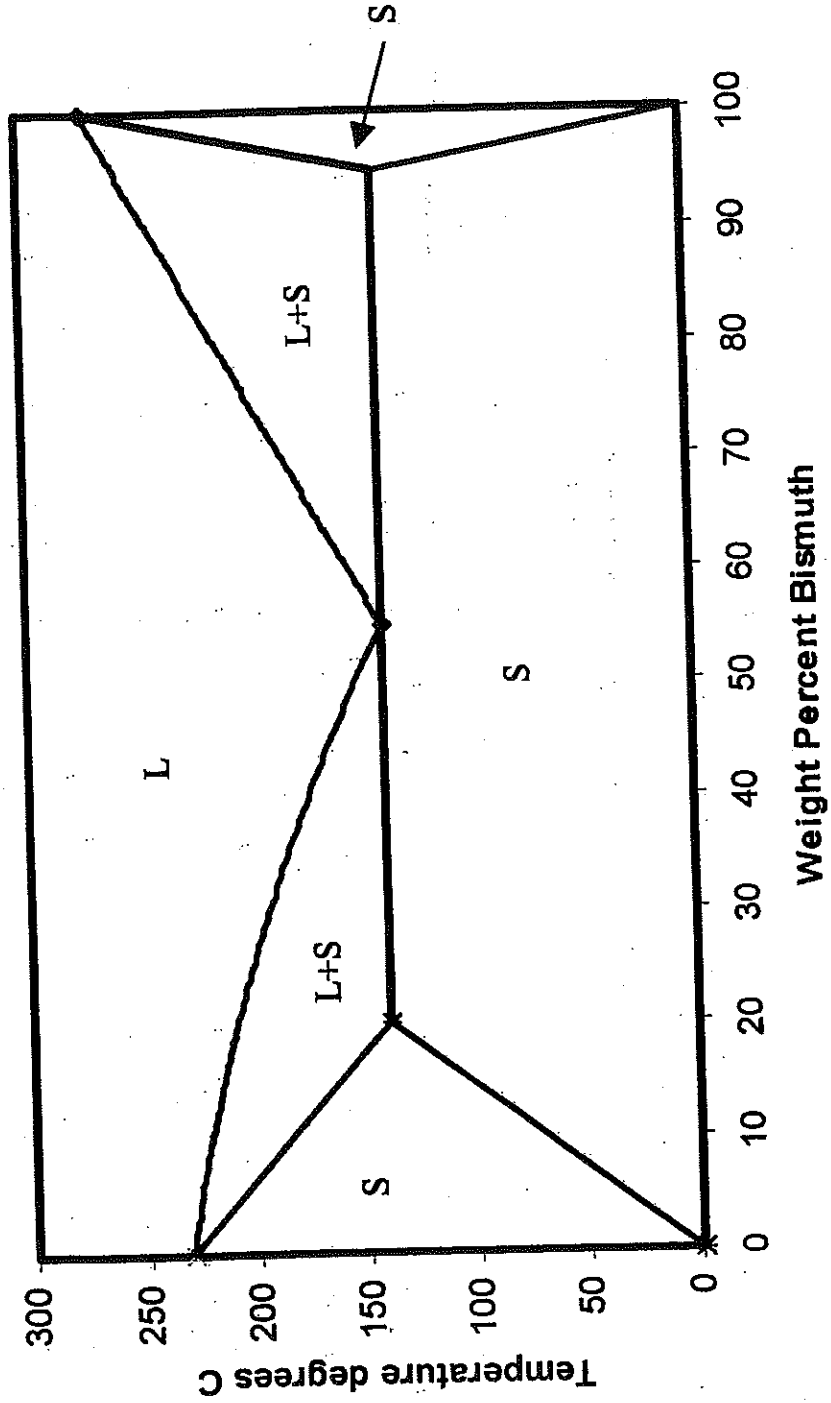
**Figure 14**  
Binary phase diagram for aluminum and zinc

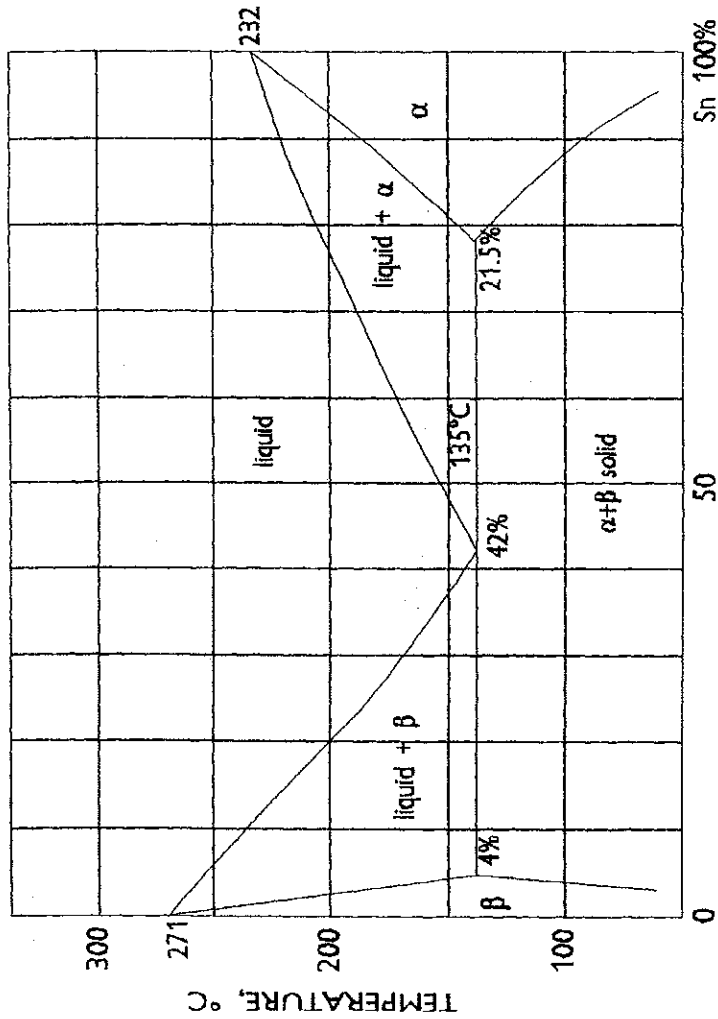
41-m



A binary phase diagram for lead and tin

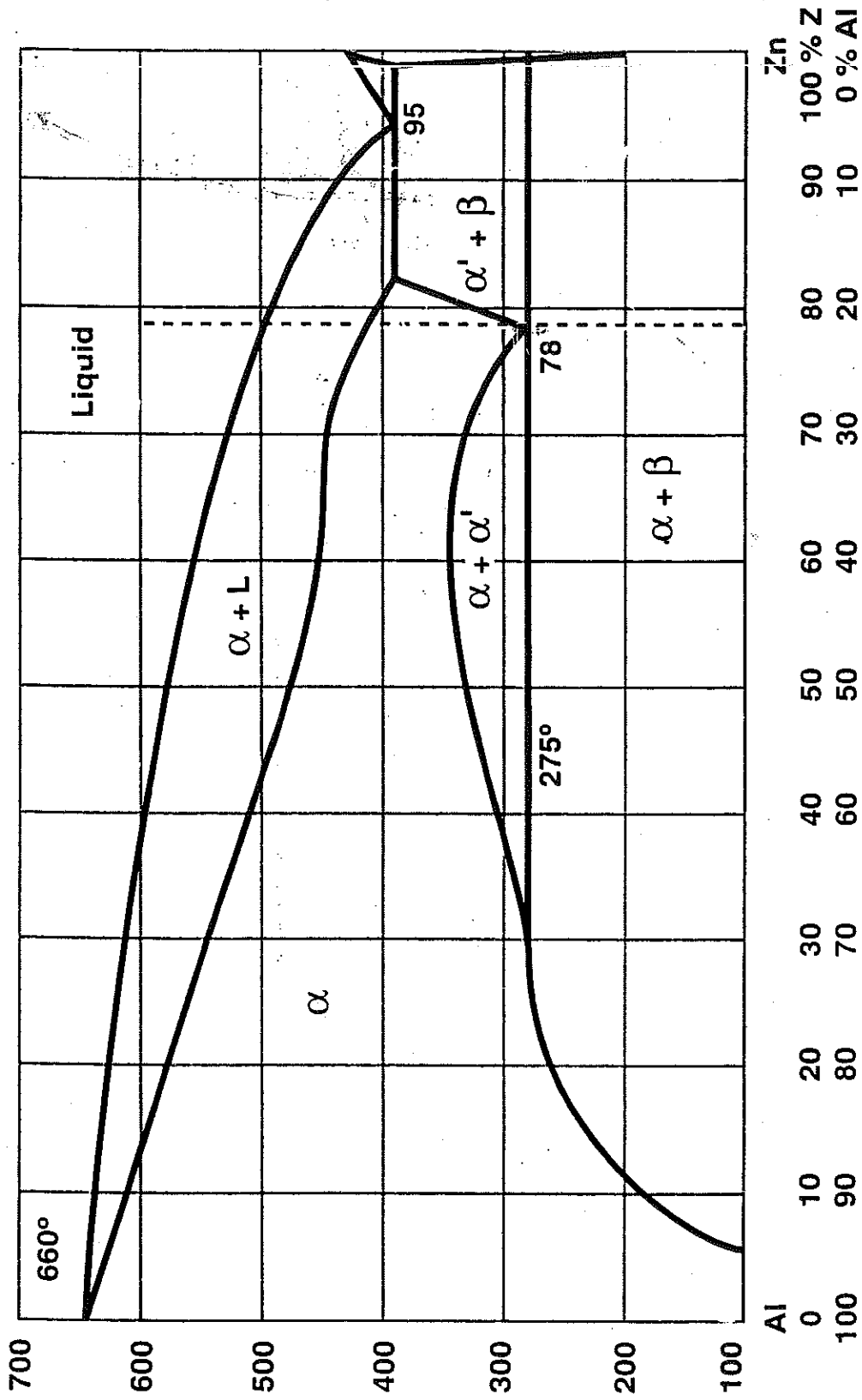
Binary Eutectic Phase Diagram  
for Bi - Sn





**Fig. 1 THE BISMUTH-TIN PHASE DIAGRAM**

The diagram is based on published data (e.g. M. Hansen & K. Anderko, 'Constitution of Binary Alloys'; C.J. Smithells, 'Metals Reference Book'). There is a slight uncertainty in the eutectic composition, with most reports in the range 42-43% tin.

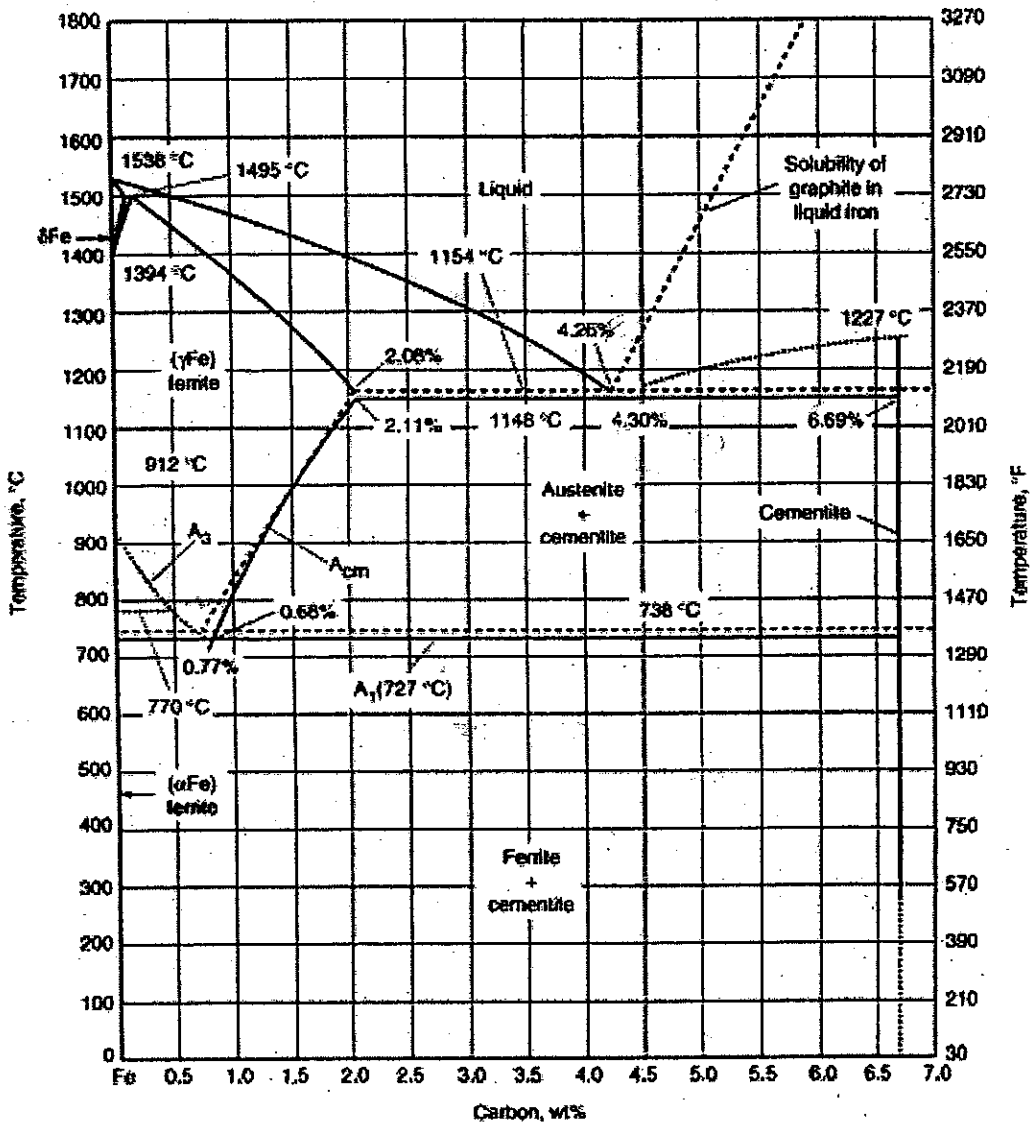


% Composition (By Weight)

**Figure 14**  
Binary phase diagram for aluminum and zinc

45-m

# Additional Fe phase diagram



Courtesy of ASM International.

46-m

**Table 1**  
Various Alloys and Phases of Iron and Steel

Name	% Carbon (by weight)	Characteristics
Ferrite	0-0.025	BCC iron; fairly soft and ductile
Pearlite	0.8	A mixture of ferrite and cementite
Cementite	6.67	Iron carbide, Fe <sub>3</sub> C Very hard and brittle
Austenite	0-2.11	FCC form of iron and steel; Normally occurs only at temperatures >727 °C
Martensite	0.02-2	Made by rapidly quenching austenite Hard and brittle
Cast Iron	2-5	Very brittle Not considered steel

## Developing the Activity Series

**Overview:** The students will develop their own activity series of metals based on lab results. Qualitative observations will be used. Tie-ins include single-replacement reactions (SRR), oxidation-reduction, practical applications such as galvanization, and predicting reactions. Students work in teams to determine the relative reactivity of six different metals in a solution of copper sulfate. My students have already covered and have an understanding of atomic structure and bonding before performing this lab.

**Goal/Objective:** The students will develop an activity series based on their own lab observations and will use it to predict and explain single replacement reactions and oxidation-reduction.

Here is the website where all of the NACE corrosion labs can be found.

[http://www.nace-foundation.org/programs/images\\_programs/cKit\\_experiments.pdf](http://www.nace-foundation.org/programs/images_programs/cKit_experiments.pdf)

### Materials/Equipment (per team):

test tube rack with six test tubes

small samples of 6 different metals:

- (1) zinc - zinc metal strips from Flinn
- (2) lead - lead metal strips from Flinn
- (3) aluminum - aluminum metal strips from Flinn
- (4) tin - tin metal strips from Flinn
- (5) magnesium - an inch of ribbon
- (6) iron - flattened wire

copper sulfate solution (0.2 M works well)

steel wool for cleaning metal samples of oxidation



## Basic Procedure:

1. Pour approximately 5 mL (or 1 inch) of "blue stuff" (copper sulfate solution) into each test tube.
2. Clean the 6 metal samples with steel wool to remove any oxidation.
3. Put a different metal sample in each of six test tubes one at a time so initial observations can be made.
4. Record observations in your journal for approximately 5 to 10 minutes. Look for signs that a chemical reaction is occurring:
  - gas bubbles being produced
  - temperature changes
  - changes in color
  - a solid precipitate forming
  - solid disintegrating
5. Rank the metals in order of reactivity.
6. Clean-up.

Class Discussion - see notes below.

Teacher demo: Place a strip of copper foil in a test tube with 7 mL of 0.1M silver nitrate solution. Have students write observations. Have them place silver in their activity series.

## Notes:

Aluminum is a very active metal but is slow to start in this lab. Aluminum oxide bonds so tightly to the surface of the metal that it is difficult to clean off. Adding sodium chloride jump starts the reaction like a catalyst. Add a little NaCl to the copper sulfate solution prior to the start of the lab (approximately 1.5 to 2 grams per 100 mL of .2M copper sulfate solution). This allows the aluminum to "behave" according to the actual activity series and does not affect the placement of the other metals. Teachers can decide whether or not to discuss the addition of the salt with their students based on their goals and objectives and the level of the students. After the students perform the lab, you may wish to show them two different aluminum trials, one with salt added to the copper sulfate solution and one without.

As your students perform the lab and write observations in their journals the teacher will need to do a little "troubleshooting". The students usually think the metals are "rusting". The teacher will need to give guidance to get them to realize that it is copper metal being formed - not rust.

Following is sort of a guideline as to how we lead the class discussion about the lab results.

Ask the students which metal they think is most reactive. They usually get this one right. It is magnesium. So I write it at the top of the chalkboard. Then we talk about which one is next. I often have to mediate because all the groups don't always agree on the order of ranking. I use "majority rules" as a guideline and it almost always works. Lead and tin can be difficult to distinguish because neither one reacts much. Here is the final ranking to be agreed upon:

Magnesium  
Aluminum  
Zinc  
Iron  
Tin  
Lead

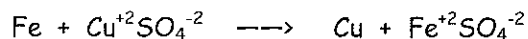
After you agree on this list, tell the students that they have left out a metal. This usually confuses them because they had six metal samples and there are six elements on their list. At this point you can tell them what the "blue stuff" is - copper sulfate. With encouragement they come up with the missing metal - copper. Ask them where it goes on the list. Most are usually not sure. Thus, you begin your discussion of what really happened in the test tubes: a single-replacement reaction involving oxidation-reduction.

Put a sample equation on the board such as:



Ask them to fill in the products. They realize that copper was formed, so somehow iron and copper switched places.

Finish the equation using ions this time:



The sulfate is unchanged. Iron went from an atom to a positive ion (define oxidation at this time) and copper went from a positive ion to a neutral atom (define reduction). It may be helpful to define a single-replacement reaction at this point.

Now try to make a connection that they will understand. You use a 1 to 10 scale to rate the metals. Here is how you explain what is occurring in the oxidation-reduction reaction.

50-m

The lovely Miss Sulfate attends a school dance with Mr. Copper. Now Mr. Copper isn't exactly the finest guy. He is only about a 3 on the 1 to 10 rating scale. When Mr. Iron (who happens to be about a 6 on the scale - definitely a more handsome, popular fellow) walks into the dance without a date, Miss Sulfate wastes no time in getting rid of Mr. Copper and getting together with Mr. Iron. Who wouldn't trade a 3 for a 6? Mr. Copper is "reduced" to being alone - no charge - no attraction - no date. Mr. Iron became "charged" when he walked in the door (was oxidized) by giving his unwanted electrons to Mr. Copper which is what reduced him. Now Miss Sulfate is attracted to Mr. Iron because of his opposite charge and they are now a couple while Mr. Copper has to wait in the singles line all alone (elemental atoms of copper). Iron can "force" his unwanted electrons onto the copper ions because iron is more reactive than copper.

This gets the students' attention. You can then use another equation to see if they are getting a handle on the concept. It is good to use zinc or magnesium. The students help you finish the equation once you write the reactants on the board. Now you can finish "rating" the metals. Here are the numbers to use:

- 10 magnesium
- 9 aluminum
- 7 zinc
- 6 iron
- 5 tin
- 4 lead

Now the students are ready to place copper on the chart in the proper location. Since copper got "replaced" (dumped as the students will tell you) in every test tube - he must be at the bottom of the list. So we add copper to the bottom as a "3".

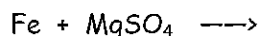
The next question you can pose to the students is this:

"Is Mr. Copper doomed to be in the singles line forever????? Can he ever hope to get a date while the other "guys" (metals) are around???"

The answer is yes if we can find a "2" or a "1". At this point you can do the teacher demonstration using a copper strip and silver nitrate. The students love this reaction. Good news for Mr. Copper. Mr. Silver is less reactive and will be reduced (replaced) by Mr. Copper. So, copper can steal silver's date (Miss Nitrate) and he is left alone to hang around by himself. We add silver to the list as a "2". By now of course the students want to know who "1" is (the real loser!!). And the answer is gold or platinum. Usually someone will think to ask if there is anyone higher than a 10. The answer is yes. Examples are calcium, sodium, and potassium. This can lead to a discussion of the periodicity of elements on the periodic table. The one who can steal a date from anyone else??? Mr. Francium. You can find clips on YouTube that show various alkali metals being placed into water. Flinn Scientific has a 37 minute video available entitled "Sodium: A Spectacular Event" that is very good.

At this point you can put a few more equations on the board that represent the reactions that occurred in class and ask the students to label which "participants" are being reduced and which are being oxidized.

Then you can throw in an equation such as this one:



Ask the students to predict what will happen. The correct answer is "no reaction". Iron is less reactive than magnesium (lower on the scale) and therefore cannot steal away the sulfate from magnesium. A "6" will not take away the "girl" from a "10".

Now you can try to interject practical applications of this concept. One is the galvanization of steel or iron metal. Ask the students to explain how a more reactive metal (zinc) can protect a less reactive metal (iron). The fact that zinc is more reactive IS the reason why it works. Zinc acts as a "sacrificial". Zinc will react with the oxidizing agent before iron. Oxidized zinc will form a tough, protective coating on the outside of the steel or iron, thus keeping the oxygen (or oxidizer) away from the iron. Oxidized iron does not make a protective coating because it flakes off exposing new iron to be oxidized. The use of sacrificial zinc, aluminum, or magnesium in a hot water heater is another practical example. This concept can also lead to a discussion of methods used to extract (reduce) metals from their ores. We follow up this lab by doing a copper oxidation/reduction lab that simulates reclaiming copper from an ore.

Metals are usually reclaimed from their ores in one of two ways: chemical reduction (using carbon in the form of coke) or electrolytic reduction (using electricity). Carbon is a relatively cheap way to reduce metals from their ores. Carbon fits on the activity series scale between aluminum and zinc - you can assign it a rating of "8". Thus chemical reduction using coke is a viable option for metals below carbon on the activity series. Metals that are more active than carbon use electrolytic reduction. Aluminum is the most abundant metallic element in Earth's crust but has become widely used only in the past century because of the difficulty in extracting it from its ore - it requires an abundant source of cheap hydroelectric power. It is much cheaper to recycle aluminum than to extract it from its ore.

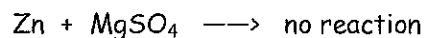
Another practical example that is easy to use involves a coffee can and a tomato sauce can. The inside of the tomato sauce can looks different than the inside of the coffee can. The tomato sauce can is galvanized to protect the steel from the acid in the tomato sauce (hydrogen is less reactive than iron). The coffee can is not galvanized because it does not contain an acid. Pineapple juice cans are also galvanized. Other contextual examples include galvanized grain bins, nails, and zinc tabs on ships or boats. Corrosion Experiment #4 - Poly Coat - investigates the need for a polymer liner inside soda cans to protect the aluminum metal from the carbonic acid in the soda.

Another quick demonstration that also illustrates the different activities of metals is to "burn" a piece of magnesium ribbon, a sample of steel wool, and a copper strip or sheet using either a propane torch or a Bunsen burner.

Heat a copper sheet with a propane torch and it will oxidize. Touch the tip of the inner blue cone of the flame to the hot copper sheet and it will actually reduce the copper oxide on the surface - it is "stealing" the oxygen away to help the propane burn. Pull the tip of the flame away from the surface and the copper will immediately oxidize as the air hits it. The different colors in the oxidation are due to the thickness of the oxidation layers.

As a final write-up for this lab, have the students discuss the following in their journals:

1. Explain oxidation and reduction using an example from the lab. Include these terms: oxidation, reduction, atom, and ion. Also, include an equation.
2. Explain why putting zinc into magnesium sulfate would NOT produce a reaction.



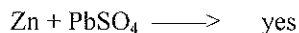
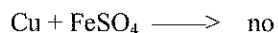
Additional assessment questions may include the following:

1. Use the activity series of metals list to predict whether or not the following reactions will occur. (Answer "yes" or "no" for each reaction.)



2. Explain (justify) your answers to question #2.
3. List 3 indications that a chemical reaction is occurring.
4. Explain how a more reactive metal like zinc can be used to "protect" a less reactive metal like iron. Give a practical example of this.
5. Zinc metal could be used in the process to claim (reduce) many metals from their ores. List three metals that zinc can replace (reduce).
6. Do metals prefer to be oxidized or reduced? Defend your answer.
7. Are most metals found in the ground in a pure state (as a metallic element) or as compounds? Explain why.
8. Predict whether magnesium is more likely to be reclaimed (reduced) from its ore by chemical reduction or electrolytic reduction. Justify your answer.

1. Use the activity series of metals list to predict whether or not the following reactions will occur. (Answer “yes” or “no” for each reaction):



2. Explain (justify) your answers to question #2.

$\text{Al} + \text{AgNO}_3 = \text{yes}$ , reaction will occur = aluminum is more reactive than silver therefore it will oxidize as it causes the reduction of silver, the aluminum will replace the silver since silver is lower on the activity series

$\text{Cu} + \text{FeSO}_4 = \text{no}$ , a reaction will not occur = copper is less reactive than iron therefore it will not replace it, copper cannot cause the reduction of iron

$\text{Zn} + \text{PbSO}_4 = \text{yes}$ , a reaction will occur = zinc is more reactive than silver therefore it will oxidize as it causes the reduction of lead, the zinc will replace the lead since lead is lower on the activity series

3. List 3 indications that a chemical reaction is occurring.

- Bubbles (gas) produced
- Temperature change
- Precipitate forms (new solid appears)
- Solid disintegrates (is “eaten” away as opposed to dissolved)
- Color change
- Odor produced
- Light emitted

4. Explain how a more reactive metal like zinc can be used to “protect” a less reactive metal like iron. Give a practical example of this.

Since zinc is more reactive than iron, zinc will be “attacked” and oxidized first. Once all of the zinc is oxidized, then the iron will be oxidized. Zinc can be used to coat iron or used as a sacrificial. Galvanized metal is an example of using a protective coat. Iron or steel is coated with zinc. The zinc oxidizes and forms a tough ceramic coating that protects the metal underneath from being oxidized as long as it isn't scratched through to expose the metal beneath. Iron does not make a protective coating when it oxidizes, the oxidation flakes off and exposes new metal to be oxidized. A water heater has a rod of either magnesium, aluminum, or zinc inserted into the tank. This rod acts as a sacrificial to protect the steel case forming the outside of the tank. The rod made out of a more reactive metal is preferentially oxidized thus protecting the steel tank.

5. Zinc metal could be used in the process to claim (reduce) many metals from their ores. List three metals that zinc can replace (reduce).

- Iron
- Tin
- Lead
- Copper
- Silver

6. Do metals prefer to be oxidized or reduced? Defend your answer.

Metals prefer to be oxidized. Metals obtain a stable number of electrons in their outermost shell (achieve the octet) when they are oxidized. Metals have an unstable number of electrons (1, 2, or 3 valence electrons) when they are reduced and in their elemental form.

7. Are most metals found in the ground in a pure state (as a metallic element) or as compounds? Explain why?

Most metals are found in the ground as a compound – in ore. Metals in compound form are oxidized which is their preferred state. Therefore most metals have to be “won” from their ore in a reduction process. Reduced metals are pure elements and only a few are found this way in nature. Metals found in the elemental state in nature are referred to as “native metals” and can include gold, silver, and copper. Most copper is found in ore however.

8. Predict whether magnesium is more likely to be reclaimed (reduced) from its ore by chemical reduction or electrolytic reduction. Justify your answer.

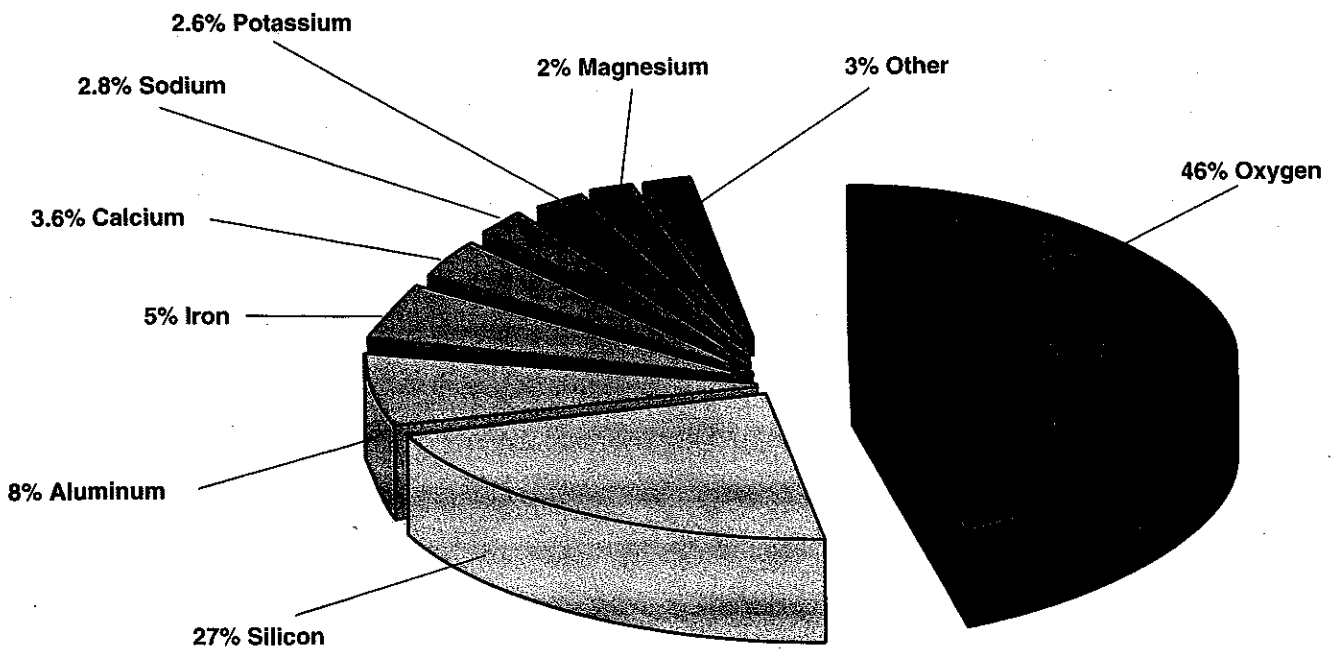
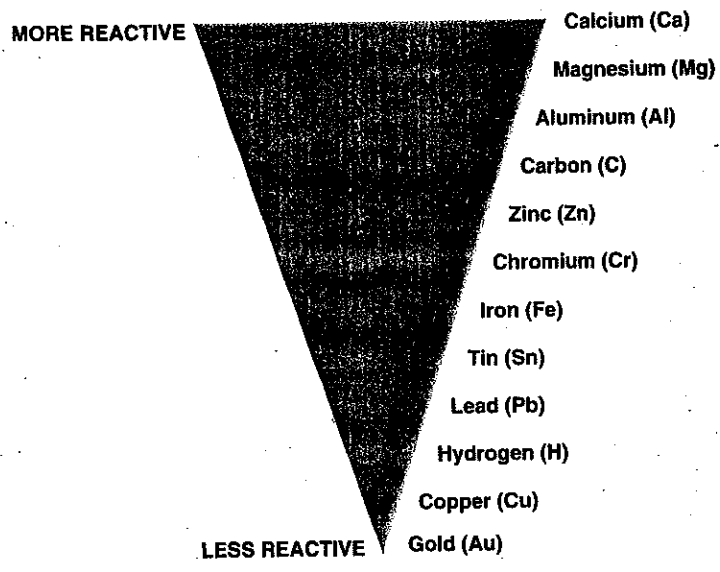
Magnesium is more likely to be reclaimed from its ore by an electrolytic reduction process. Metals which are less reactive than carbon can be cheaply reduced from their ore by chemical reduction using coke (a form of carbon). Metals that are more reactive than carbon are reduced from their ore by using electricity on molten or dissolved ore. Since magnesium is more reactive than carbon (as shown by the activity series), it is reclaimed from ore by electrolytic reduction.

Here is the website where all of the NACE corrosion labs can be found:

[http://www.nace-foundation.org/programs/images\\_programs/cKit\\_experiments.pdf](http://www.nace-foundation.org/programs/images_programs/cKit_experiments.pdf)

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SS-M



**Figure 12**  
 Weight percentage's of the most common elements in the earth's crust

56-m



METAL	Li	K	Na	Ca	Mg	Al	Mn	Zn	Cr	Fe	Cd	Co	Ni	Sn	Pb	H	ANTIMONY	BISMUTH	ARSENIC	COPPER	MERCURY	SILVER	PLATINUM	GOLD		
SYMBOL	Li	K	Na	Ca	Mg	Al	Mn	Zn	Cr	Fe	Cd	Co	Ni	Sn	Pb	H	Sb	Bi	As	Cu	Hg	Ag	Pt	Au		
ATOMIC NO.	3	19	11	20	12	13	25	30	24	26	48	27	28	50	82	1	51	83	33	29	80	47	78	79		
ATOMIC WT.	6.94	39.1	22.99	40.08	24.31	26.98	54.94	65.37	52.0	55.85	112.4	58.93	58.71	118.7	207.2	1.008	121.8	209.	74.92	63.54	200.6	107.9	195.1	197.0		
VALENCE+																										
EASE OF REDUCTION	VERY DIFFICULT																EASY						VERY EASY			
REDUCED BY	ELECTROLYSIS OF FUSED HYDROGEN, OXIDE OR CHLORIDE																CARBON WITH DIMINISHING DIFFICULTY						HEAT FROM OXIDES			
OXIDATION IN AIR	OXIDIZE RAPIDLY OR BURN IN AIR																OXIDIZE WITH COMPARATIVE EASE						DO NOT OXIDIZE			
ACTIONS ON WATER AND ACIDS	LIBERATES HYDROGEN FROM WATER						LIBERATES HYDROGEN FROM STEAM AND ACIDS						LITTLE ACTIONS ON ACIDS						LIBERATES NO HYDROGEN FROM ACIDS. REACTS WITH OXIDIZING ACIDS ONLY.						NO ACTION ON PURE ACIDS	
OCCURANCE IN NATURE	COMBINED FORM ONLY																FREE AND COMBINED FORM ONLY						FREE			
BOILING PT. °C	1336	760	892	1440	1110	2450	2150	906	2665	3000	765	2900	2730	2270	1725	2527	1380	1560	613	2595	357	2210	4530	2970		
MELTING PT. °C	181	63.7	97.8	838	651	660	1245	419	1875	1536	321	1495	1453	232	327	233	630.5	271	sublime	1083	-38.4	960.8	1769	1063		
DENSITY	.53	.86	.97	1.55	1.74	2.70	7.43	7.13	7.19	7.87	8.65	8.90	8.9	7.3	11.36	0.0898	6.62	9.80	5.72	8.96	13.55	10.49	21.45	19.32		
SYMBOL	Li	K	Na	Ca	Mg	Al	Mn	Zn	Cr	Fe	Cd	Co	Ni	Sn	Pb	H	Sb	Bi	As	Cu	Hg	Ag	Pt	Au		

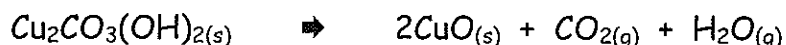
57-3

**Copper Metal from Malachite Earth Resources**

The lab was taken from the following reference. The entire article is available to read if you wish.

Yee, G., Eddleton, J., and Johnson, C. (December 2004). Copper Metal from Malachite circa 4000 B.C.E. Journal of Chemical Education, Vol. 81 No. 12, pgs. 1777-1779. Retrieved from www.JCE.DivCHED.org.

This lab extracts the copper from an ore with the mineral malachite, basically copper carbonate hydroxide  $\text{Cu}_2\text{CO}_3(\text{OH})_2$ , as people may have done it, more primitively, at the beginning of the copper age, about 4000 B.C.E. We are using malachite jewelry beads. The malachite is changed to solid (s) copper (II) oxide and two other products that are released as gases (g): carbon dioxide and water. (Copper can form two different ions,  $\text{Cu}^{1+}$  and  $\text{Cu}^{2+}$ . The (II) indicates the  $\text{Cu}^{2+}$  ion.) The following is the chemical equation showing the reactant or starting material on the left of the arrow and the products on the right of the arrow.



The copper (II) oxide,  $\text{CuO}$ , is heated with carbon,  $\text{C}$ , to reduce the copper oxide to copper metal,  $\text{Cu}$ , as shown in the following chemical equation:



Step One: Weigh out five small (2mm diameter) beads (work in groups of three). Record weight.

Step Two: Roasting.

The beads are placed in a crucible and the crucible is covered with a lid and placed in a ceramic triangle on a ring stand. A Bunsen burner is used to roast the sample for 15 min. The height of the ring should be adjusted such that the tip of the inner blue cone of the Bunsen burner is touching the bottom of the crucible. *Caution: at the beginning of the heating, the sample can sometimes behave like popcorn and jump out of the crucible as the hot gases escape, so it must be covered.*

Step Three: Cool and Weigh. After this period, the heat is removed and the crucible is allowed to cool for 10 min, yielding copper(II) oxide. Note that the bead is brittle at this point, so extra care should be taken when handling it. The sample is reweighed and the mass of the  $\text{CuO}$  is recorded. Record Weight.

Step Four: Reduction.

About 1/4 of a charcoal briquette is placed into a folded paper towel and finely crushed with a hammer. The roasted  $\text{CuO}$  sample is returned to the crucible. The crucible is filled with crushed charcoal to within 1/4 inch of the top and tapped gently to help settle the contents. The crucible is covered and heated on the Bunsen burner for 20 - 45 min (longer time better). *Caution: carbon monoxide gas might be produced.*

Step Five: Cool, Clean, and Weigh. The heat is removed and the crucible is allowed to cool, covered, for 10 min. The excess charcoal is removed and the copper metal isolated by spreading it out in the paper pan. If the sample appears red and chalky, it has not been reacted fully and should be reacted further. The product can be brushed to dislodge any charcoal particles adhering to the metal. Wiping the bead on a paper towel also works to remove the weakly adherent carbon layer. Throw the carbon ash into the recycle bag. The product is weighed.

Step Six: Calculations

(1) Find the weight of malachite by adding up the atomic weights of all the atoms in the formula. Find the weight of copper in the malachite formula. Calculate the percent weight of copper (theoretical %). (2) Find the percent weight of copper you extracted from your malachite beads (experimental %). (3) Find the percent error and discuss what could cause the error. (4) Repeat for copper oxide.

Step Seven: Characterization.

Find the density of your final product and compare to the density of copper. Hit the bead with a hammer and see if it is malleable (Caution: be sure to wear your safety goggles). Test with a conductivity meter to see if the bead conducts electricity.

**COPPER FROM MALACHITE PRE-LAB**

Read the entire handout containing the background and lab procedure. Answer the following questions.

Questions	Record answers here:
1. Give the chemical name and formula for the copper compound in the green mineral Malachite.	
2. How long do you need to roast the bead?	
3. During the roasting step, the copper compound in malachite is converted into a new product. Give the chemical name and formula for the copper-containing product.	
4. What does the (II) designate in the name for CuO, copper (II) oxide? Why is it used?	
5. Besides the bead, what is added to the crucible for the reduction step?	
6. How long will the bead need to be heated for the reduction step?	
7. Give the chemical name and formula for the product of the reduction step.	
8. List the three ways that the final copper product will be characterized.	

**LAB WORKSHEET** (You may transfer this to a separate piece of paper if you need more room.)

Step 1: Weight of five (5) malachite beads \_\_\_\_\_

Observations: \_\_\_\_\_

Step 2: Observations during roasting step: \_\_\_\_\_

Step 3: Weight of copper oxide (CuO): \_\_\_\_\_

Observations: \_\_\_\_\_

Step 4: Observations during the reduction step: \_\_\_\_\_

Step 5: Weight of copper (Cu): \_\_\_\_\_

Observations: \_\_\_\_\_

Step 6: Theoretical Calculations

Atomic Weight of malachite:

Weight of copper in malachite:

Percent copper in malachite:

Experimental Calculations

Percent copper extracted:

Percent error:

Sources of error:

Repeat Step 6 for copper oxide for extra credit.

Step 7: Density (Describe method and record measurements):

Malleability test:

Conductivity test:

59-m

## ELECTROPLATING A NAIL

### MATERIALS:

100 mL beaker  
Copper Strip  
Salt – several tablespoons  
Vinegar – 80 mL  
Nail – box bright  
2 lengths of wire with alligator clips  
Power Supply

### PROCEDURE:

1. Pour vinegar into beaker.
2. Pour 1 TBSP salt into vinegar.
3. Stir
4. Create a “saturated solution” (adding salt until there is salt residue on beaker’s bottom.)
5. Bend copper and hang on edge of beaker. More copper in the beaker is better.
6. Attach alligator clip onto copper on outside of beaker. (Not in the vinegar!)
7. Attach clip from the second wire onto the nail and hang into solution.
8. Attach free end of each wire to the power supply
9. Set the power supply to 6 Volts.
10. Write your observations of the solution in your logbook.
11. As each 5 minutes pass, look at the nail and write your observations in your logbook.
12. After no more changes are observed, write your observations of the nail and the solution.
13. Put away your materials.

### QUESTIONS:

1. What happened to the solution? \_\_\_\_\_  
\_\_\_\_\_
2. What do you see on the nail? ? \_\_\_\_\_  
\_\_\_\_\_
3. What do you see on the copper? \_\_\_\_\_  
\_\_\_\_\_
4. When would electroplating be useful? \_\_\_\_\_  
\_\_\_\_\_
5. Name some products that use electroplating? \_\_\_\_\_  
\_\_\_\_\_

# LOST WAX CASTING (EASY)

By Len Booth

This is a modification of the more complex lost wax casting process. It is designed so that it can all be done with a hot plate or a normal kitchen stove. See the PowerPoint located on the CD for pictures of the process.

## Materials & Equipment

- ▶ Hot Plate 1
- ▶ Balance 1
- ▶ Bolt cutter or hack saw 1
- ▶ Plastic Tarp 1
- ▶ Crucible tongs 1
- ▶ Mixing Container 1
- ▶ Stir Stick (Paint stick) 1
- ▶ Measuring Cup 1
- ▶ Wax Paper 1
- ▶ Gloves (cloth) 1
- ▶ Glass Rod 1
- ▶ Candle 1 - to heat wax to attach the sprue
- ▶ Aluminum Foil 1 or Metal Lid - for melting wax from flask
- ▶ Wax - I use soy wax from IASCO
- ▶ Mold - A candy mold from Michaels (craft shop)
- ▶ Can - for melting wax
- ▶ Straw 2 (sprue wax is an option)
- ▶ Sticky wax - obtain from jewelry supply (Rio Grande)
- ▶ Can (with both ends removed) - a 12 oz can works well
- ▶ Silicone Caulking 3 (clay is an option)
- ▶ Caulking gun 3 (not needed if using clay option)
- ▶ Petroleum Jelly 3 (not needed if using solid foam for base)
- ▶ Plaster of Paris
- ▶ Tin
- ▶ Ceramic Crucible (or metal can)
- ▶ Hammer
- ▶ Bucket - for washing plaster of Paris from mixing container

## Footnotes for Materials

- ▶ 1: These are typically used elsewhere in MST
- ▶ 2: Cast wax into these to form sprues. The wax is easily removed from the straw by pushing with a glass stirring rod. An option would be to purchase sprue wax.
- ▶ 3: These are used to form a sprue base for the steel can used as a flask. (See slide #23.) One alternative is to use a foam square with a mound of silicone. A second option is to use a foam square with a mound of clay.

61-m

## Procedure

- ▶ Melt wax in a container on the hot plate
- ▶ Do not let the wax heat above 180°F
- ▶ Carefully cast the melted wax into the mold
- ▶ Allow the wax to completely cool
- ▶ Remove the wax model from the mold
- ▶ Attach 2 pieces of sprue wax to it
- ▶ Cut the sprue wax to an appropriate length
- ▶ Mass the model with sprue attached
- ▶ Attach the other end of the sprue wax to the Casting Flask Base.
- ▶ An alternative method for attaching the model to a sprue base is to use a lump of clay on a slab of Styrofoam
- ▶ Mix plaster of Paris according to directions (usually 2 parts plaster of Paris to 1 part water). Try using 2 cups plaster of Paris for a 12 oz can.
- ▶ Carefully pour this mixture into the casting flask until it is 2 - 3 cm above the wax model
- ▶ Tap on the flask side to attempt to remove any air bubbles
- ▶ Let the flask with plaster of Paris set over night
- ▶ Remove the flask base
- ▶ Use the mass of your wax model and sprue that you found earlier
- ▶ Calculate 30% of this value
- ▶ Add this 30% to the mass of the wax model and sprue
- ▶ This new total mass helps allow for a "button"

### SAMPLE WAX CALCULATIONS

- ▶ Mass of wax and sprue = 8.2 g
- ▶ Find 30%:  $8.2 \text{ g} \times 0.30 = 2.46 \text{ g}$
- ▶ Mass of model, sprue, & button:  
 $8.2 \text{ g} + 2.46 \text{ g} = 10.66$
  
- ▶ Determine the mass of tin needed by multiplying the mass of the wax model, sprue, and button by the specific gravity of tin which is 7.29.
- ▶ The wax has a specific gravity of about 1.
- ▶ Since tin is 7.29 times as dense as the wax, you need 7.29 times as much tin (by mass) than you have wax.

### SAMPLE METAL CALCULATIONS

- ▶ Mass of model, sprue, & button:  
 $8.2 \text{ g} + 2.46 \text{ g} = 10.66 \text{ g}$
- ▶ Mass of tin needed:  
 $10.66 \text{ g} \times 7.29 = 77.7 \text{ g}$
  
- ▶ Place this flask in a metal container (can or aluminum foil) with the sprue hole down
- ▶ Set this in an oven or on a hot plate at about 200oF for at least 1 hour
- ▶ This should cause the wax to melt
- ▶ Remove the flask from the oven (hot plate)

- ▶ Increase the temperature to 350°F
- ▶ Replace the can with the melted wax with a clean can (or aluminum foil)
- ▶ Place the flask and new can in the oven (hot plate) for at least 1 hour
- ▶ This will allow the mold to heat to a temperature closer to that of tin's melting pt.
- ▶ Mass the amount of tin that you need
- ▶ Place the tin in a ceramic crucible or a metal can
- ▶ Heat the tin until it melts
- ▶ Put on a pair of cloth gloves
- ▶ Remove the flask from the oven (hot plate.)
- ▶ Place the flask with the sprue side up on a heat resistant surface
- ▶ Carefully cast (pour) the tin into the mold
- ▶ Let the flask cool for at least 5 minutes
- ▶ It can then be cooled in a bucket of water
- ▶ Remove the casting from the flask and plaster of Paris. This can be done by placing on a plastic tarp and hitting the flask with a hammer.
- ▶ Separate your product from the sprue by using either a hack saw or bolt cutters.
- ▶ Touch up the product if necessary
- ▶ ENJOY!!

#### STEPS FOR MAKING A FLASK BASE OF SILICONE

- ▶ Place a heavy coat of petroleum jelly on the bottom edge of the can to be used as a flask
- ▶ Place a thick layer (at least  $\frac{1}{4}$  inch) of silicone caulking on a sheet of wax paper (This layer should be slightly larger than the diameter of the can that will act as the flask)
- ▶ Build a mound of caulking at least 1 inch high in the center of the layer
- ▶ Imbed the can slightly into the caulking
- ▶ Allow the caulking to dry at least one day
- ▶ Remove the can and clean off the petroleum jelly

- activity series:** also known as the Electromotive Force Series. This is a listing of the elements according to their potential differences and ability to place other elemental ions in solution.
- alloy:** a substance that has metallic properties and is made up of two or more chemical elements, of which at least one is a metal.
- annealing:** a heat treatment of a metal designed to produce a soft, ductile condition. Typically the metal is heated and allowed to cool slowly.
- anode:** electrode at which electrons are released during corrosion. The half reaction at the anode is called oxidation and the metal is said to be oxidized. The anode is the electrode that disintegrates during corrosion.
- bronze:** An alloy composed of tin and copper.
- cathode:** electrode which accepts electrons during corrosion. The half reaction at the cathode is called reduction and the metal is said to be reduced. The cathode is not destroyed during corrosion.
- cathodic protection:** a more active metal is placed next to a less active metal. The more active metal will serve as an anode and will be corroded instead of the less active metal. The anode is then called a sacrificial anode.
- cold-working:** a permanent deformation of a metal below its crystallization temperature. Deforming the metal creates more dislocations which entangle, pinning them and thereby strengthening the metal.
- corrosion:** oxidation-reduction reaction where electrons are released at the anode and taken up at the cathode.
- dislocations:** linear defects in a crystal.
- ductile:** can be drawn or stretched into wire and other shapes.
- elastic deformation:** materials return to their original shape after a small load or stress is applied.
- face-centered cubic:** crystal arrangement of close-packed layers of particles where three layers of particles alternate positions. This layering is known as ABCABC.
- failure:** ultimate separation of metal parts due to applied loads, i.e., it breaks.
- fatigue:** the application and release of stresses as metal is used which cause small cracks to grow, during many cycles of application, until they fracture.
- grain:** a crystal (ordered arrangement of atoms).
- grain boundary:** the interface between the grains or crystals.
- Hall Process:** an electrolytic technique to refine aluminum from its ore.
- hardening:** heating and rapidly cooling steel.
- heat treating:** modification of properties and structure of alloys by specific heating and cooling cycles.
- hexagon closest packing (HCP):** crystal arrangement of layers of particles where two layers alternate positions. The layering is known as ABAB.
- malleable:** can be hammered into a sheet.
- martensite:** a super-saturated solid solution of carbon in ferrite. The carbon atoms distort the BCC ferrite into a BC-tetragonal structure.
- metallic bonding:** bond formed by positive ions surrounded by a sea of valence electrons.



**ore:** a natural mineral deposit that contains enough valuable minerals to make it profitable to mine at the current technology.

**oxide:** a compound of oxygen with some other chemical element.

**oxidation:** the half of an electrochemical reaction where electrons are released. Oxidation occurs at the electrode called the anode.

**pinned:** the dislocations in a crystal get tangled or attached to atoms of an alloying agent.

**plastic deformation:** materials remain deformed after a load is added and then removed.

**quenched:** cooled rapidly.

**reduction:** the half of an electrochemical reaction where electrons are taken up. Reduction occurs at the cathode.

**reduction of metals:** changing a metal ion to a neutral atom by the addition of electrons.

**steel:** an iron-carbon alloy, malleable in some temperature range as initially cast. Steel usually contains some other alloying elements such as silicon, manganese, etc. as well as impurities such as sulfur and phosphorus.

**strength:** a measure of the ability of a material to support a load.

**stress:** the internal forces produced by application of an external load, tending to displace component parts of the stressed material. It is defined as the force (load) divided by the area on which it acts.

**toughness:** the ability to absorb energy of deformation without breaking. High toughness requires both high strength and high ductility.

**unit cell:** The smallest repeating array of atoms in a crystal.