Introduction to
Biomaterials & Biocompatability
Lecture 3

Metals as Biomaterials

George L. Collins, Ph.D.
Research Professor
Medical Device Concept Laboratory
Department of Biomedical Engineering
New Jersey Institute of Technology
email: collins@adm.njit.edu

A Short History of Metals

working metals is an ancient human endeavor

Metals of Antiquity

(1) Gold (ca) 6000BC
(2) Copper,(ca) 4200BC
(3) Silver,(ca) 4000BC
(4) Lead, (ca) 3500BC
(5) Tin, (ca) 1750BC
(6) Iron,smelted, (ca) 1500BC
(7) Mercury, (ca) 750BC

Iron was available to the ancients in small amounts from meteors. There is some indication that man-made iron was available as early as 2500 B.C., however, ironmaking did not become an everyday process until 1200 BC. In the early days iron was 5 times more expensive than gold and its first uses were as ornaments. Iron weapons revolutionized warfare and iron implements did the same for farming. Iron and steel were building blocks for civilization. The utility of metals is rooted in their strength and their ablitiy to be shaped. Shaping, as opposed to casting, requires that metals be deformable.

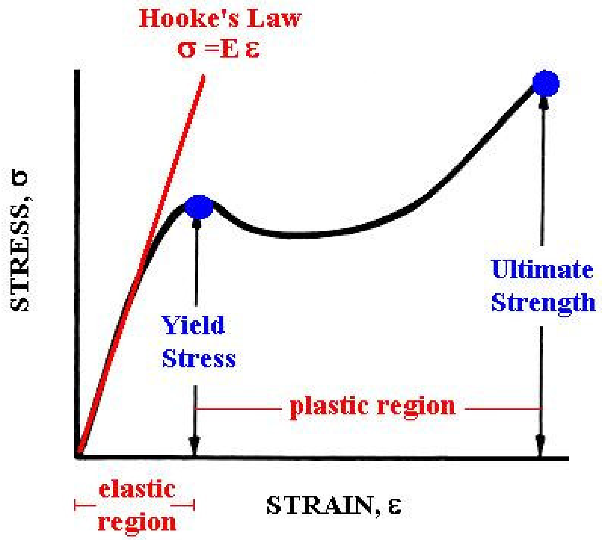
http://neon.mems.cmu.edu/cramb/Processing/history.html

Plastic Deformation

Metals undergo plastic deformation. This type of deformation is not reversible and accounts for why metals can be formed. However, an object in the plastic deformation range will first have undergone elastic deformation, which is reversible, so the object will return part way to its original shape. Soft thermoplastics have a rather large plastic deformation range as do ductile metals such as copper, silver and gold. Steel does, too, but not iron. Plastic deformation requires movement in the internal structure of a material. The atomic or molecular aggregates must rearrange as the specimen changes shape.

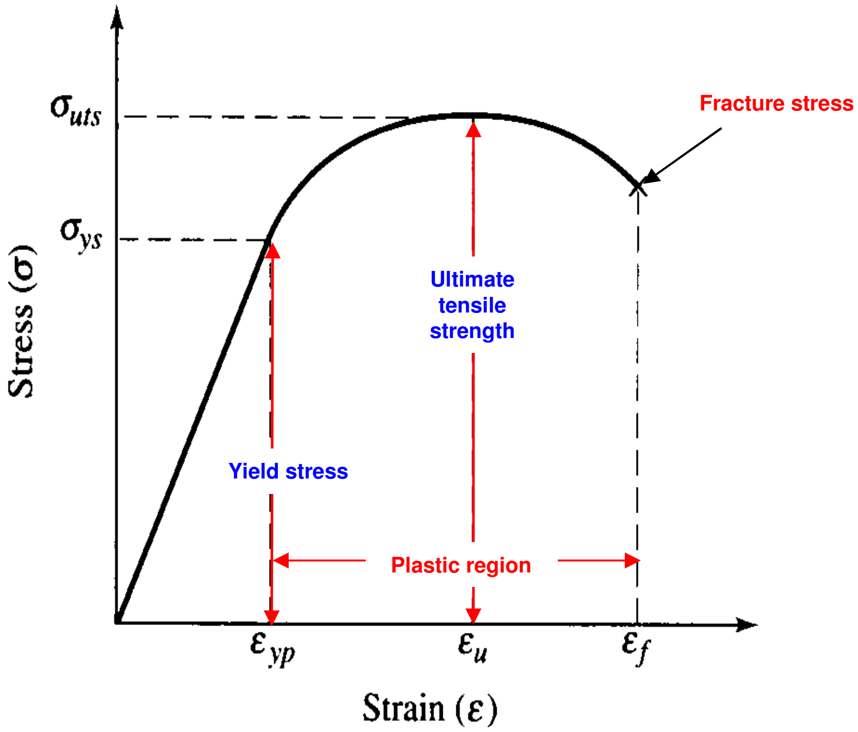
http://en.wikipedia.org/wiki/Plastic_deformation

STRESS-STRAIN CURVE FOR A TYPICAL MATERIAL



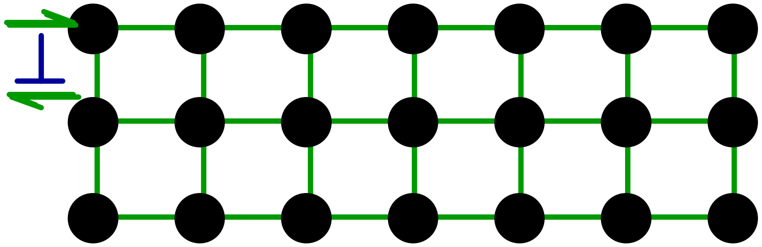
E=Modulus of Elasticity=Young's Modulus

Typical Metal

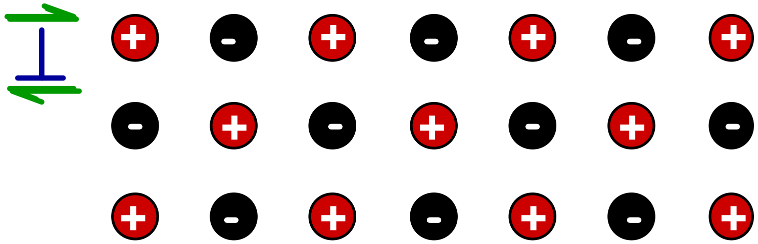


Deformation Requires Motion

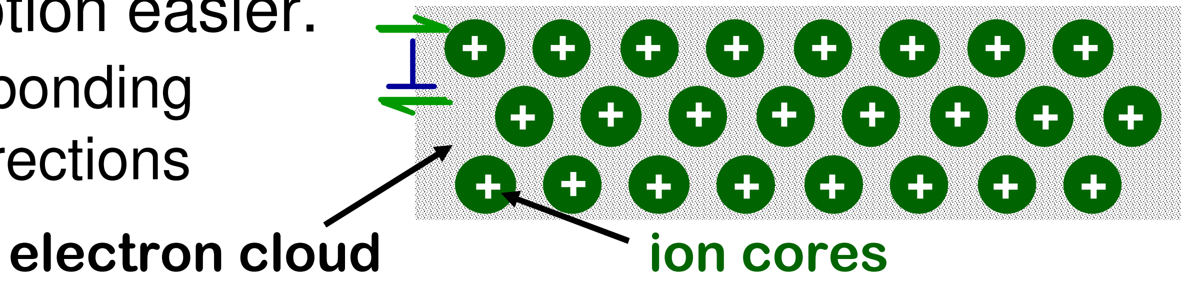
- Covalent Ceramics
  (Si, diamond): Motion hard.
  -directional (angular) bonding



- Ionic Ceramics (NaCl):
  Motion hard.
  -need to avoid ++ and --
  neighbors.

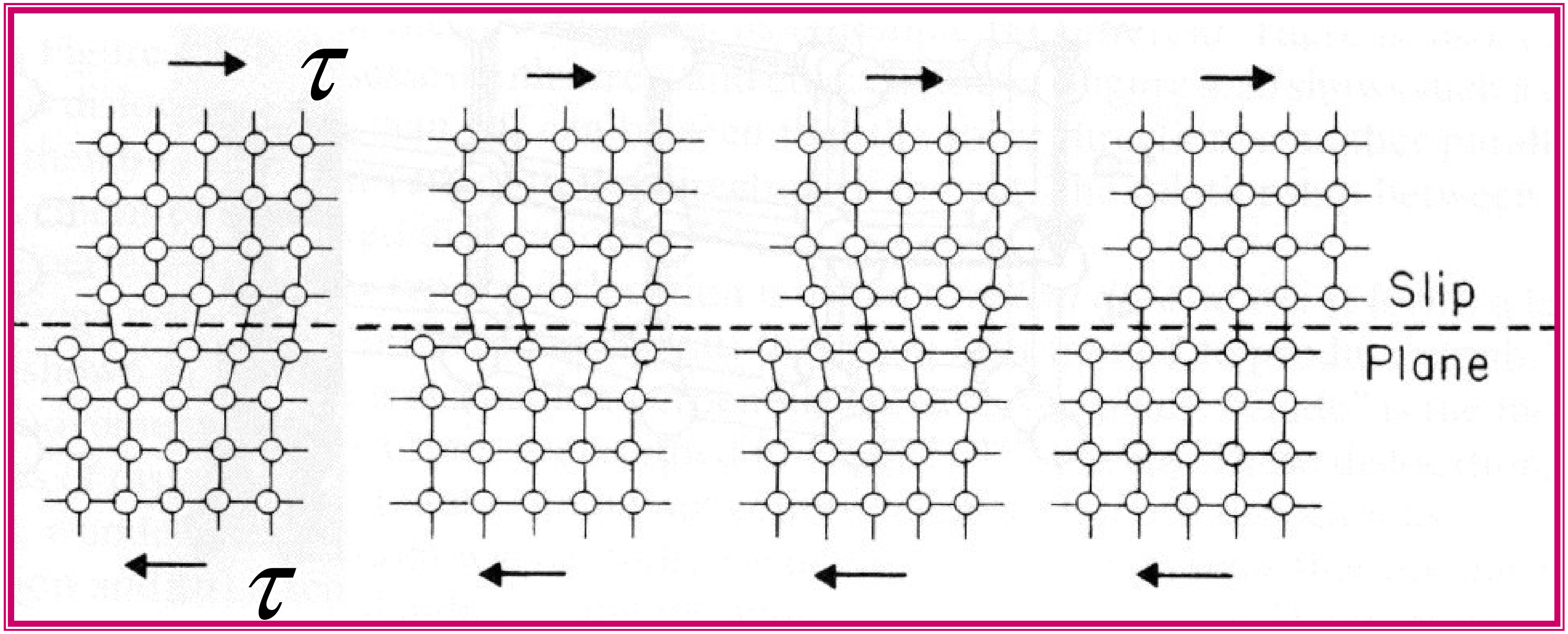


- Metals: Disl. motion easier.
  -non-directional bonding
  -close-packed directions
  for slip.

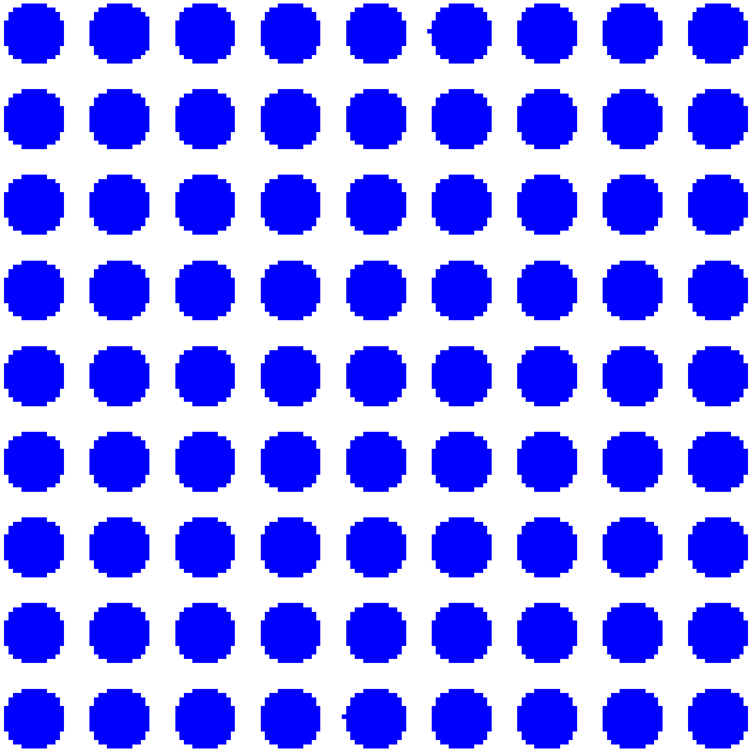


Microstructural Origins of Plasticity in Metal

- Slip, Climb and Slide of atoms in the crystal structure.
- Slip and Climb occur at Dislocations and Slide occurs at Grain Boundaries.



Plastic deformation occurs in metals by the movement of dislocations.



For *macroscopic* deformation in three dimensions, many dislocations have to move through the crystal.

http://www.tf.uni-kiel.de/matwis/amat/def_en/kap_5/illustr/a5_1_1.html

Under an applied stress, the lattice at first strains elastically and the bonds in the dislocation core region are distorted even more. Eventually, the stretched bonds in the core region break, and new bonds form between these atoms and others that are at or near the correct distance apart for an unstrained lattice. In this way, part of the crystal 'slips' one interatomic distance with respect to the other part. The process is then repeated.

Usually the bonds break and reform one at a time, so that the amount of strain energy stored in the crystal at any one time is rather small. Once the dislocation has passed completely through the crystal in this way, the lattice is left internally strain-free (the half plane has moved to the outer edge of the crystal), although the crystal itself has undergone a permanent, plastic shape change.

Plastic deformation occurs in metals by the movement of dislocations. Anything that hinders their movement increases the stress required for the onset of plastic flow.

An important aspect of the development of metal properties has been related to the control of dislocation motion.

1. Mutual interference of dislocation motion.
2. Grain boundaries as barriers to dislocation motion.
3. Solid solutions introduce local elastic strains that can hinder dislocation motion.

Strain Hardening = Work Hardening = Cold Working
Strengthening by Increase of Dislocation Density

Ductile metals become stronger when they are deformed plastically at temperatures well below the melting point. The reason for strain hardening is the increase of dislocation density with plastic deformation. The average distance between dislocations decreases and dislocations start blocking the motion of each other.

STRENGTHENING STRATEGY 1: COLD WORKING

The percent cold work (%CW) is often used to express the degree of plastic deformation:

$$\%CW = \left(\frac{A_0 - A_d}{A_0} \right) \times 100$$

where A_0 is the original cross-section area, A_d is the area after deformation.

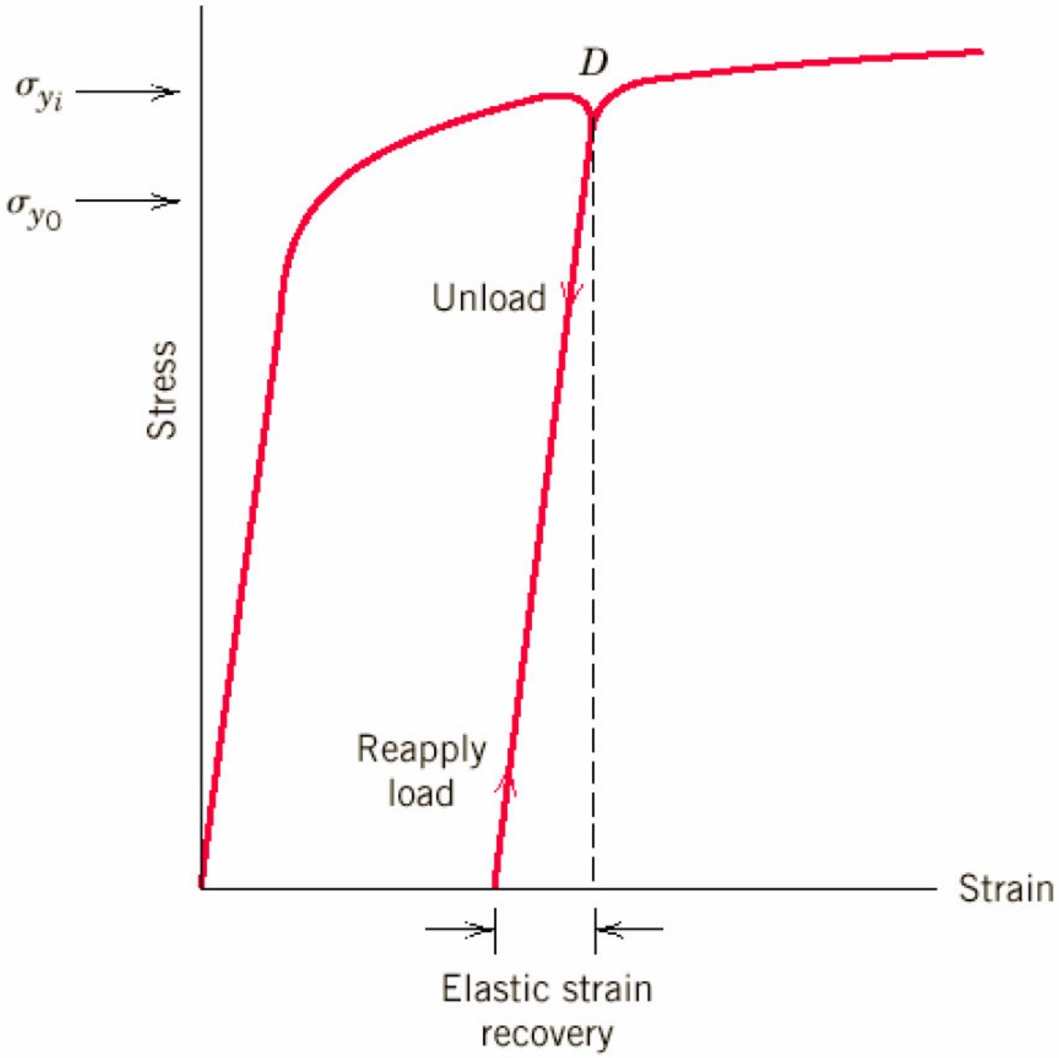
%CW is another measure of the degree of plastic deformation, in addition to strain.

Strain Hardening (II)

As plastic deformation proceeds, dislocations interact with one another making further deformation more difficult. The phenomenon is called *work- or strain-hardening*.

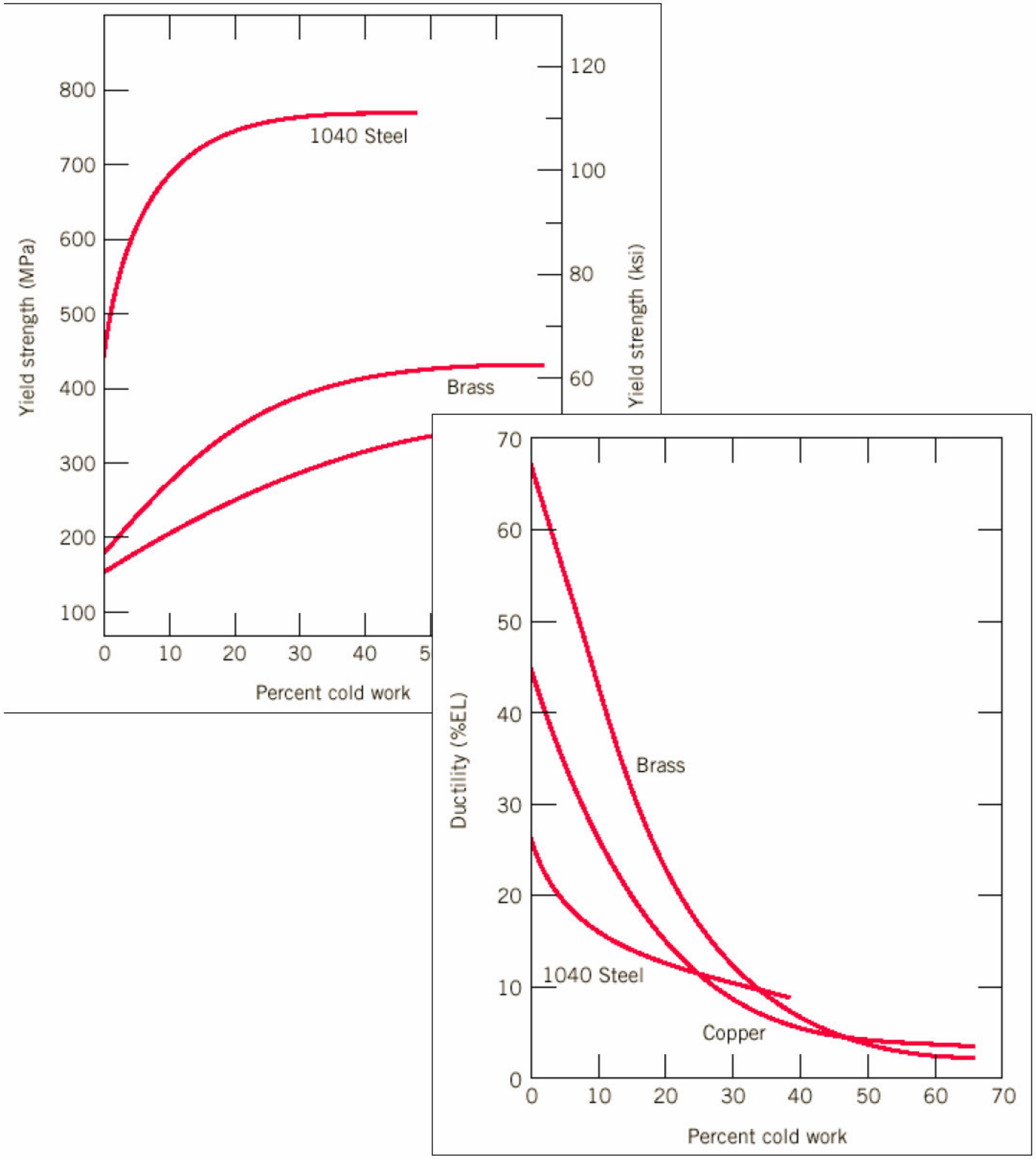
On the stress-strain curve, a sample is plastically deformed to point S and then unloaded. It will be permanently deformed by S%. On retesting, the material will not yield until the stress σ_S has been reached.

The work hardening increment decreases with strain, and increasing work hardening reduces the margin between yield and fracture.



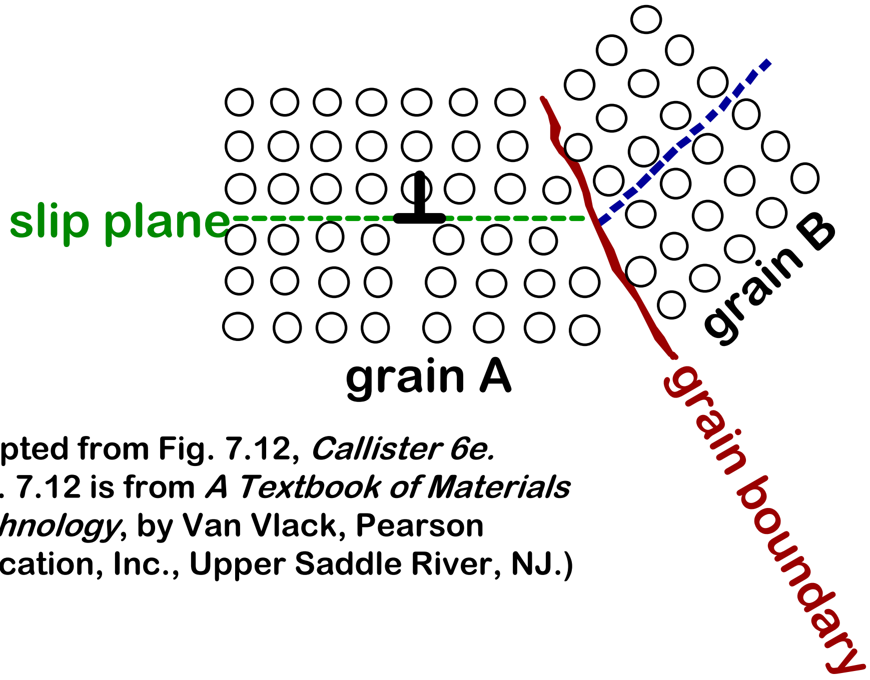
Strain Hardening (III)

Strain Hardening (IV)



STRENGTHENING STRATEGY 2: REDUCE GRAIN SIZE

- Grain boundaries are barriers to slip.
  - dislocation has to change directions
  - grain boundary region disordered, so discontinuity in slip planes
- Barrier "strength" increases with misorientation.
- Smaller grain size: more barriers to slip.



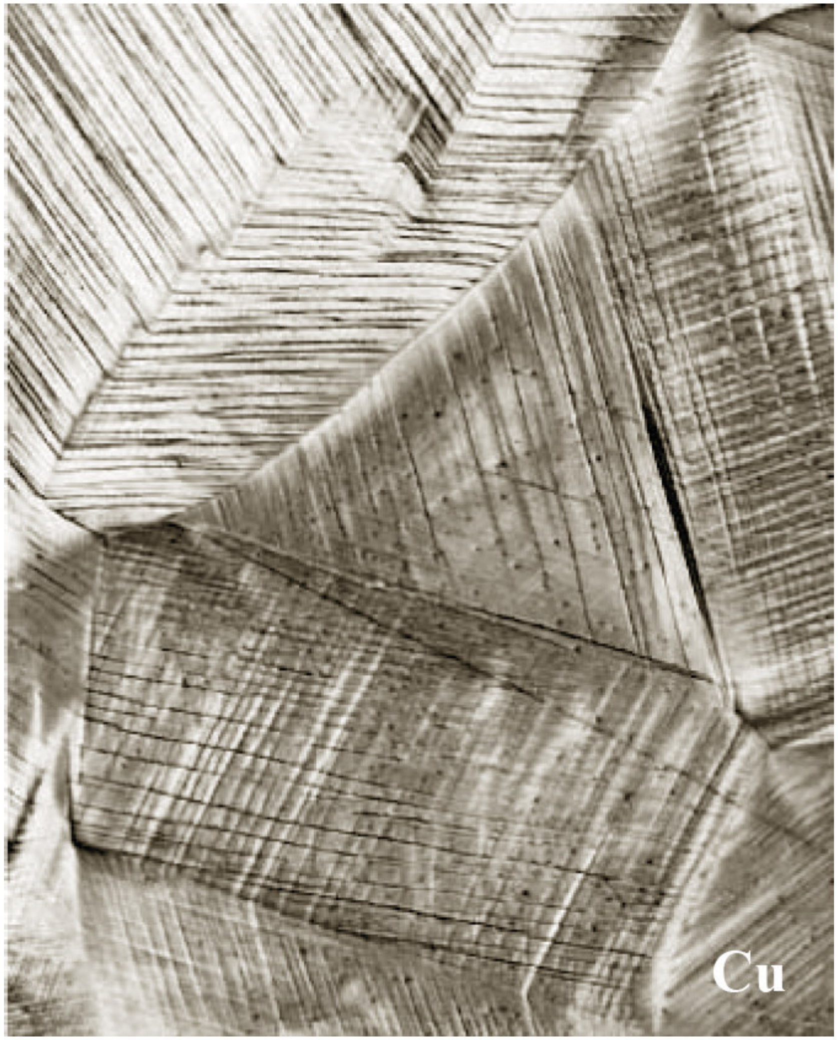
Adapted from Fig. 7.12, *Callister 6e.* (Fig. 7.12 is from *A Textbook of Materials Technology*, by Van Vlack, Pearson Education, Inc., Upper Saddle River, NJ.)

- Hall-Petch Equation:

$$\sigma_{yield} = \sigma_o + k_y d^{-1/2}$$

Strengthening by Grain Size Reduction

Dislocations cannot easily cross grain boundaries because of changes in direction of slip plane and disorder at grain boundary. As a result, polycrystalline metals are stronger than single crystals (the exception is the perfect single crystal without any defects, as in whiskers)

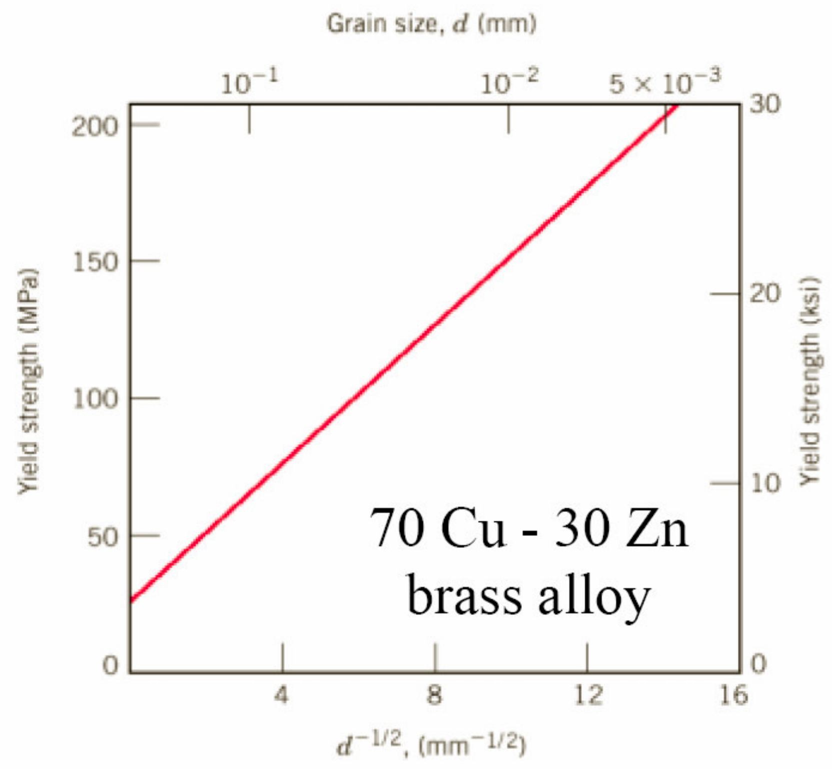


The finer the grains, the larger the area of grain boundaries that impedes dislocation motion. Grain-size reduction usually improves toughness as well. Usually, the yield strength varies with grain size d according to Hall-Petch equation:

$$\sigma_y = \sigma_0 + k_y / \sqrt{d}$$

where σ_o and k_y are constants for a particular material, d is the average grain diameter.

Grain size can be controlled by the rate of solidification,
by plastic deformation and by appropriate heat treatment.



Strengthening by Solid- Solution

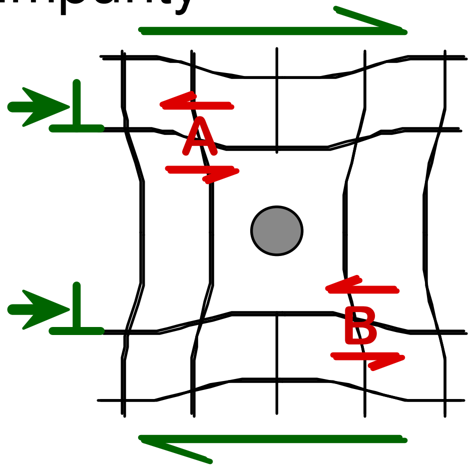
Interstitial or substitutional impurities in a solution cause lattice strain. As a result, these impurities interact with dislocation strain fields and hinder dislocation motion.

Impurities tend to diffuse and segregate around the dislocation core to find atomic sites more suited to their radii. This reduces the overall strain energy and “anchor” the dislocation.

STRENGTHENING STRATEGY 3: SOLID SOLUTION STRENGTHENING

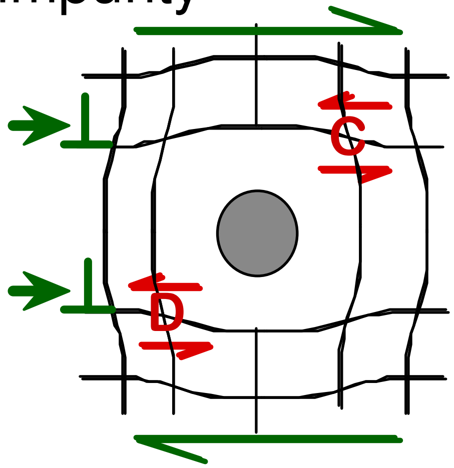
- Impurity atoms distort the lattice & generate stress.
- Stress can produce a barrier to dislocation motion.

- Smaller substitutional impurity

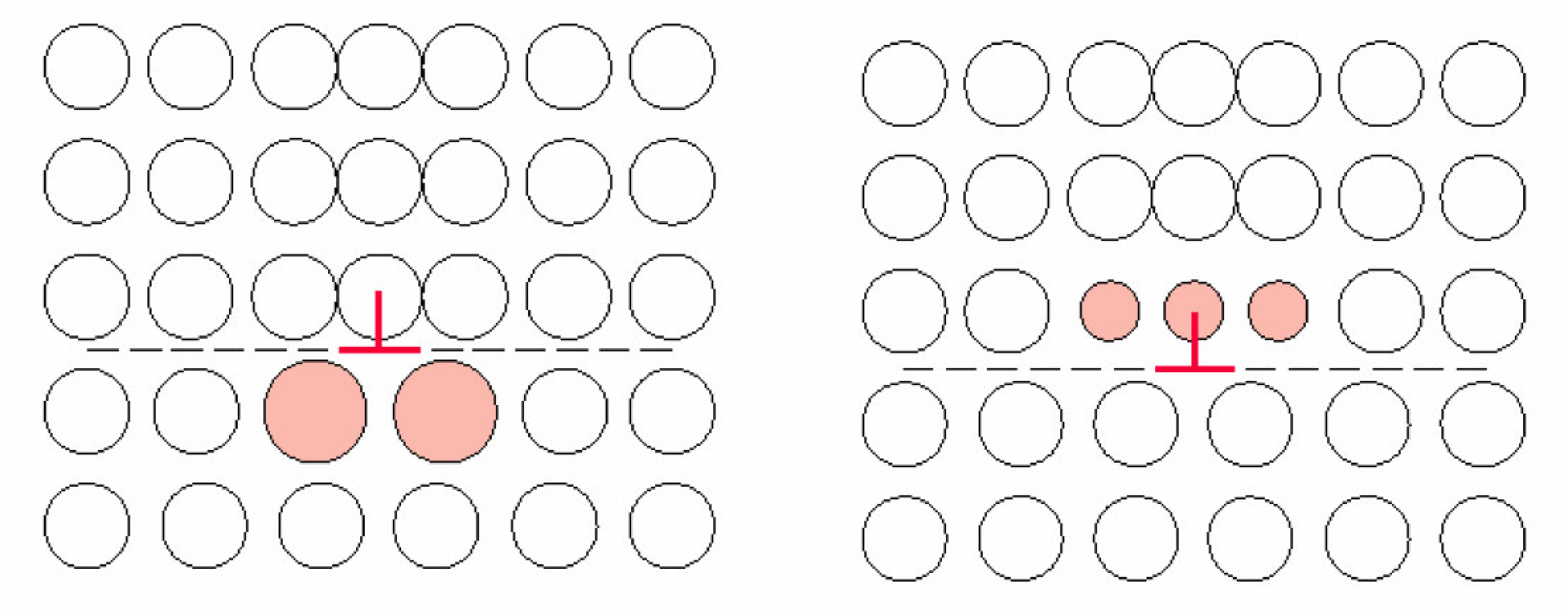


Impurity generates local shear at A and B that opposes disl motion to the right.

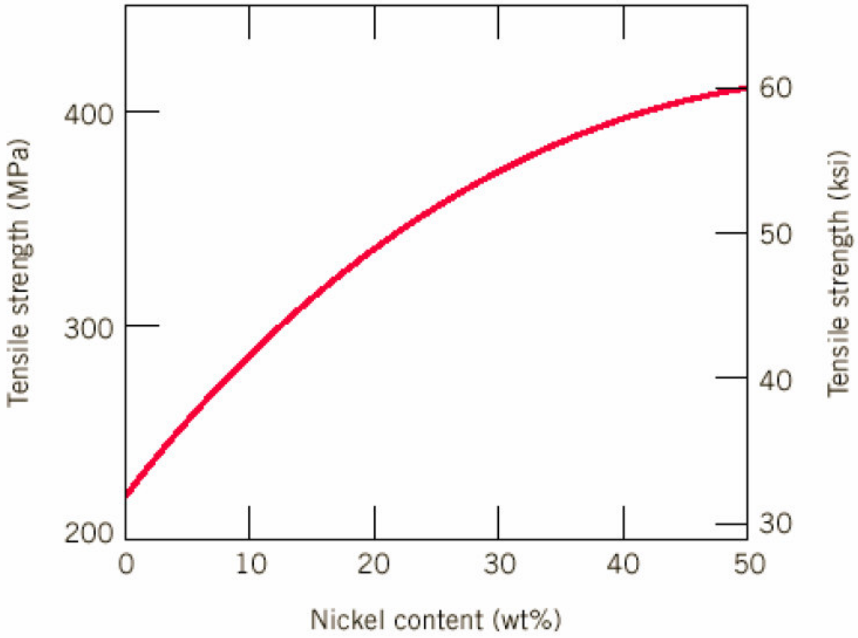
- Larger substitutional impurity

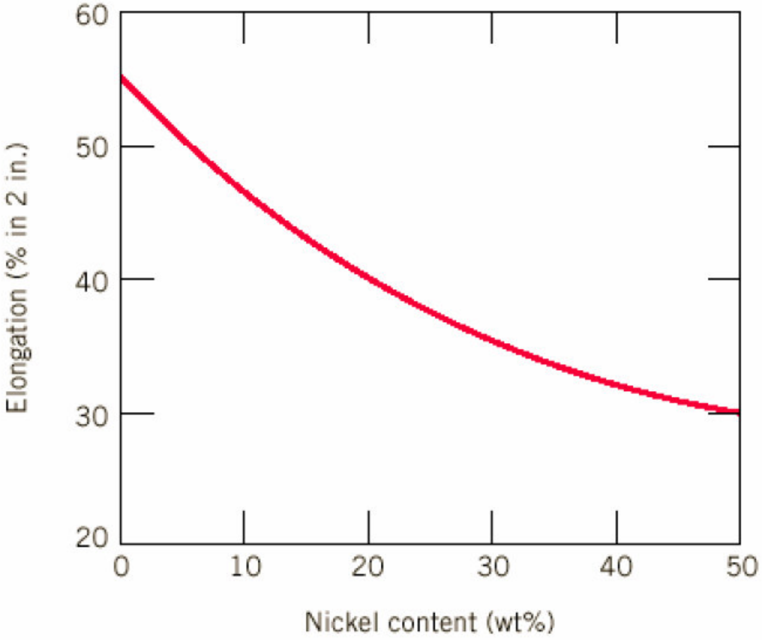


Impurity generates local shear at C and D that opposes disl motion to the right.



Smaller and larger substitutional impurities tend to diffuse into strained regions around the dislocation leading to partial cancellation of impurity-dislocation lattice strains.

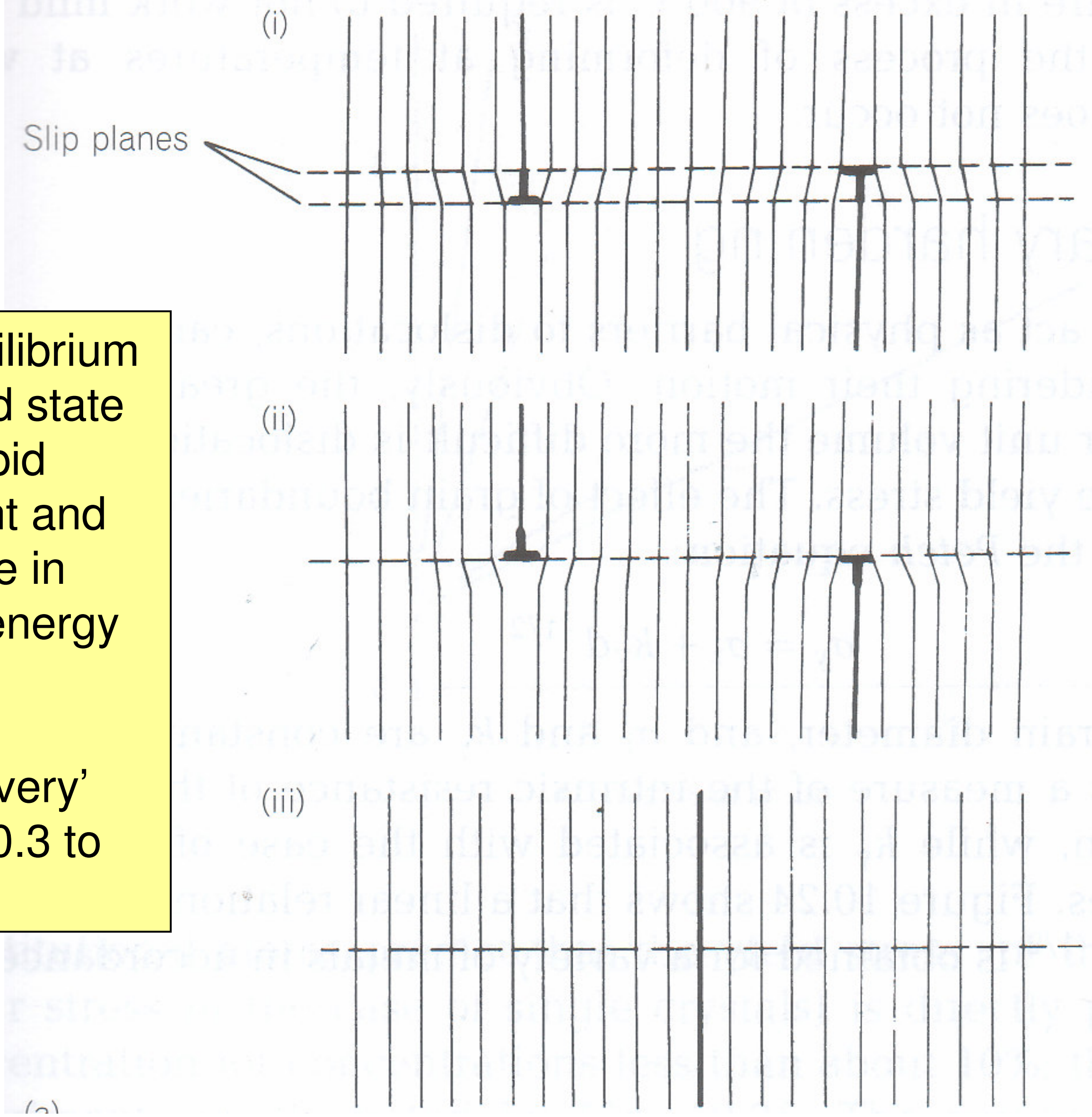

Tensile strength (MPa)
400
300
200
Tensile strength (ksi)
60
50
40
30
0
10
20
30
40
50
Nickel content (wt%)


Elongation (% in 2 in.)
60
50
40
30
20
0
10
20
30
40
50
Nickel content (wt%)

Recovery

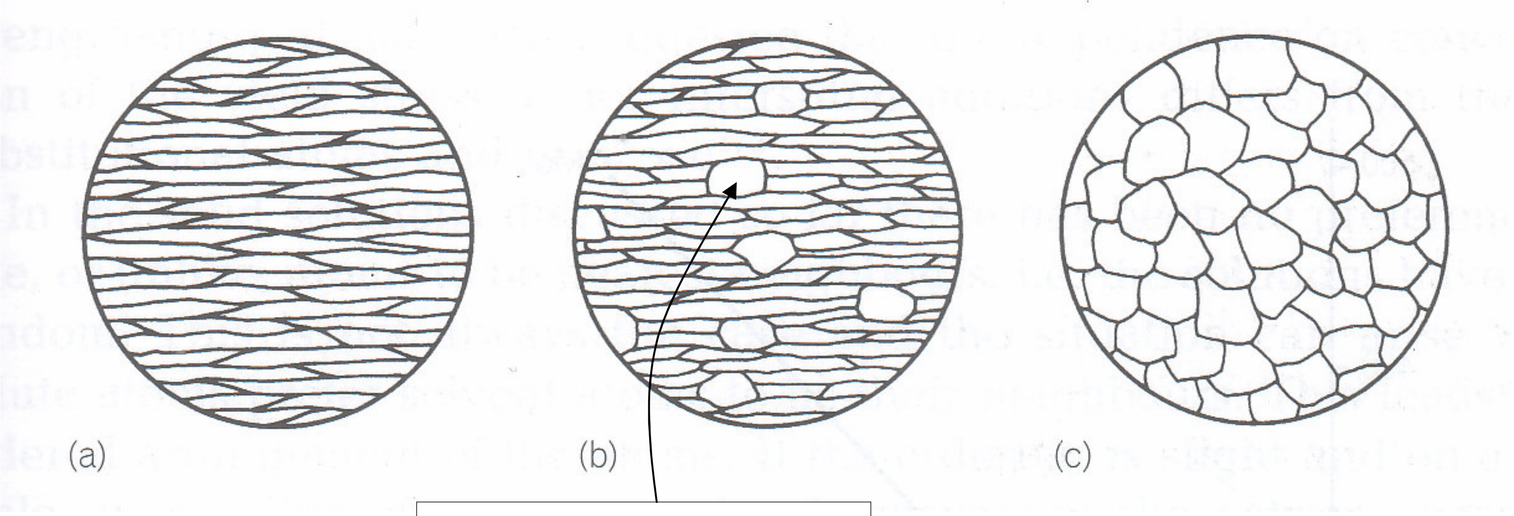
Dislocations are non-equilibrium structural features. If solid state diffusion is sufficiently rapid dislocation rearrangement and annihilation will take place in order to reduce the free energy of the material.

This process called ‘recovery’ takes place in the range 0.3 to $0.4T_m$.



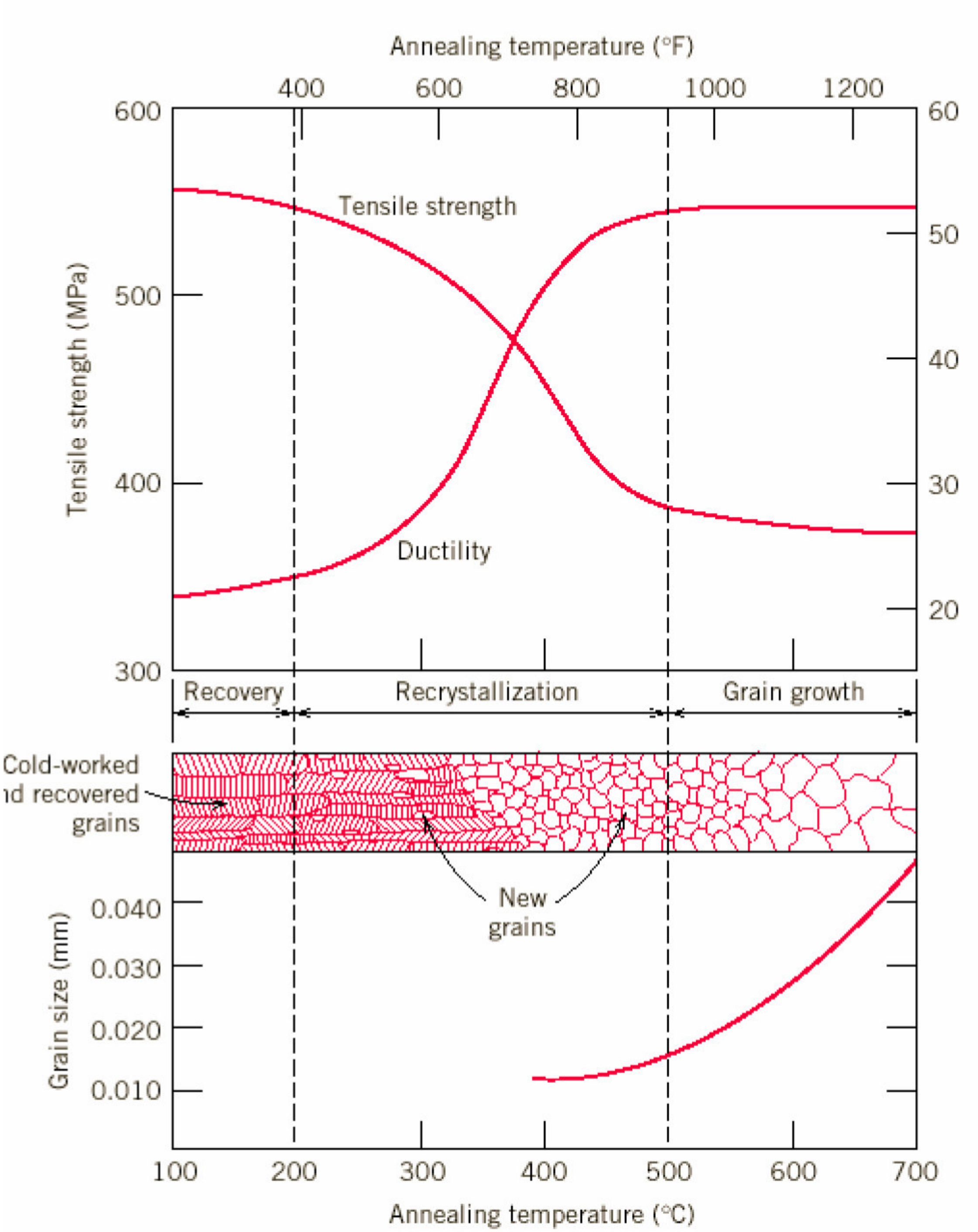
Recrystallization

Recrystallization is another mode of recovery. Recrystallization is the nucleation and growth and growth of new grains of *low dislocation density and larger grain size.*



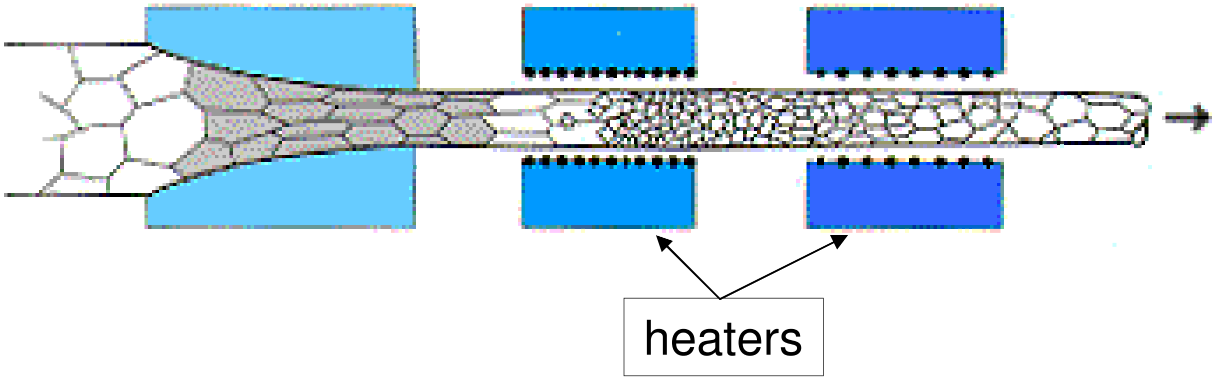
Nucleation of recrystallization

Recrystallization will result in the lowering of grain boundary area.



Annealing temperature (°F)
400
600
800
1000
1200
600
500
400
300
Tensile strength (MPa)
60
50
40
30
20
Tensile strength
Ductility
Recovery
Recrystallization
Grain growth
Cold-worked
nd recovered
grains
New
grains
0.040
0.030
0.020
0.010
Grain size (mm)
100
200
300
400
500
600
700
Annealing temperature (°C)

Metal Wire Manufacture



Bicycle spoke manufacture involves drawing rods through a series of dies of decreasing hole size until wire of the desired diameter is produced. The die imposes transverse compression while applying tension at the same time. The transverse compression increases dislocation density - a factor which strengthens the wire by strain-hardening. The accumulation of strain hardening can become too great and break the brittle wire. To avoid this, the wire is softened periodically during the drawing process. This is accomplished by heating the wire above some threshold temperature in a process known as annealing. There are three stages of annealing - recovery, recrystallization, and grain growth.

Discussion Topic:

Historically metals have been used as biomaterials because of their strength and their ability to be formed. What two factors limit the use of metals as materials in the body?

Consider…

Two important factors that impact the use of metals as biomaterials are,

1) The tendency of metals to corrode in the body environment

2) The toxicity of corrosion products

Metal Corrosion

Corrosion resistance is a crucial determinant in the selection of orthopedic appliances. Corrosion can weaken an implant so that the metal can no longer withstand normal stresses before failing. For example, stainless steel, which is particularly prone to corrosion and subsequent implant failure, is generally restricted to the fixation of fractures. In this setting, the implant needs to be functional only until the bone heals. In contrast, cobalt-chromium and titanium are used for artificial joint replacements in part because of their increased resistance to corrosion.

http://www.ajronline.org/cgi/content/full/184/4/1219

--79-year-old woman with thigh pain after fall

79-year-old woman with thigh pain after fall. Radiograph shows corrosion of screws in retained surgical plate placed 40 years earlier for femur fracture and fuzzy debris around screws.

Patterson, S. P. et al. Am. J. Roentgenol. 2005;184:1219-1222

Copyright © 2007 by the American Roentgen Ray Society

--78-year-old woman with distal humeral fracture

78-year-old woman with distal humeral fracture. Lateral radiograph shows corrosion of retained surgical screw placed in radius 12 years earlier. Note fuzziness along surface of screw.

Patterson, S. P. et al. Am. J. Roentgenol. 2005;184:1219-1222

Copyright © 2007 by the American Roentgen Ray Society

What is Corrosion?

Corrosion is a method whereby metals and alloys return to their un-refined naturally occurring forms as ores and minerals. Metals such as iron, nickel, zinc, aluminum and copper occur naturally as oxides as well as sulfides and carbonates (meaning they are combined with the elements oxygen, sulfur or carbon and oxygen). When ore is refined this natural and most stable state is reversed to produce the actual metal which is less stable under natural conditions than the ore. A large amount of energy is applied to the ore (blast furnaces etc.) as the metal is converted from its oxide, carbonate, sulfide etc. Given the right conditions and following thermodynamic driving forces, these high energy and more ordered metals tend to revert to their low energy state and less ordered ore condition.

Corrosion Theory

Corrosion is the primary means by which metals deteriorate. Most metals corrode on contact with water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes, and other solid and liquid chemicals. Metals will also corrode when exposed to gaseous materials like acid vapors, formaldehyde gas, ammonia gas, and sulfur containing gases. Corrosion specifically refers to any process involving the deterioration or degradation of metal components. The best known case is that of the rusting of steel. Corrosion processes are usually electrochemical in nature, having the essential features of a battery. When metal atoms are exposed to an environment containing water molecules they can give up electrons, becoming themselves positively charged ions, provided an electrical circuit can be completed. This effect can be concentrated locally to form a pit or, sometimes, a crack, or it can extend across a wide area to produce general wastage. Localized corrosion that leads to pitting may provide sites for fatigue initiation and, additionally, corrosive agents like seawater may lead to greatly enhanced growth of the fatigue crack.

All metals exhibit a tendency to oxidize, some more easily than others. A tabulation of the relative strength of this tendency is called the Galvanic series.

The corrosion reaction proceeds by the coupling of two primary electrochemical processes; an anodic reaction and a cathodic reaction.

$$M \rightarrow M^{2+} + 2e^{-}$$

The electrochemical process at the anode involves the release of electrons by the metal to increase its state of oxidation (oxidation).

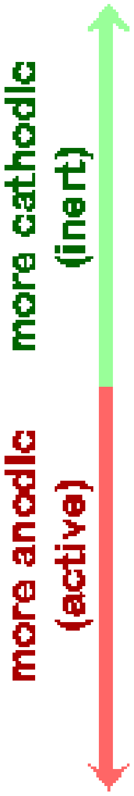
$$2e^{-} + H_2O + \frac{1}{2}O_2 \rightarrow 2OH^{-}$$

The electrochemical process at the cathode requires that the electrons liberated at the anode be taken up by some chemical moiety that can reduce its state of oxidation (reduction).

The Galvanic Series

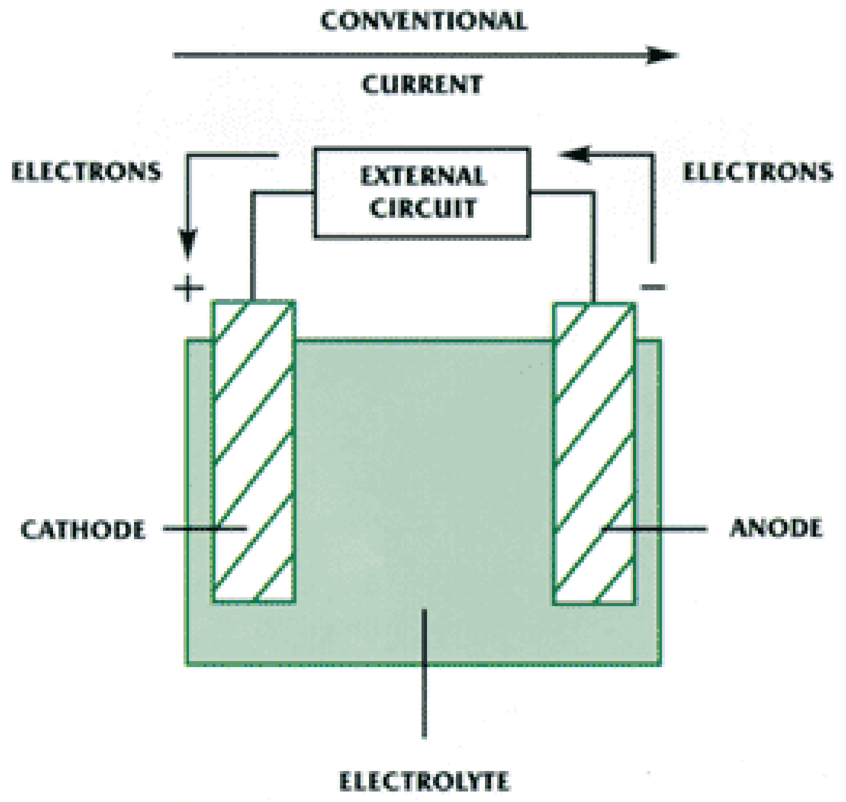
- Ranks the reactivity of metals/alloys in seawater

Metals can be ranked in terms of their relative tendencies to release electrons in anodic processes.

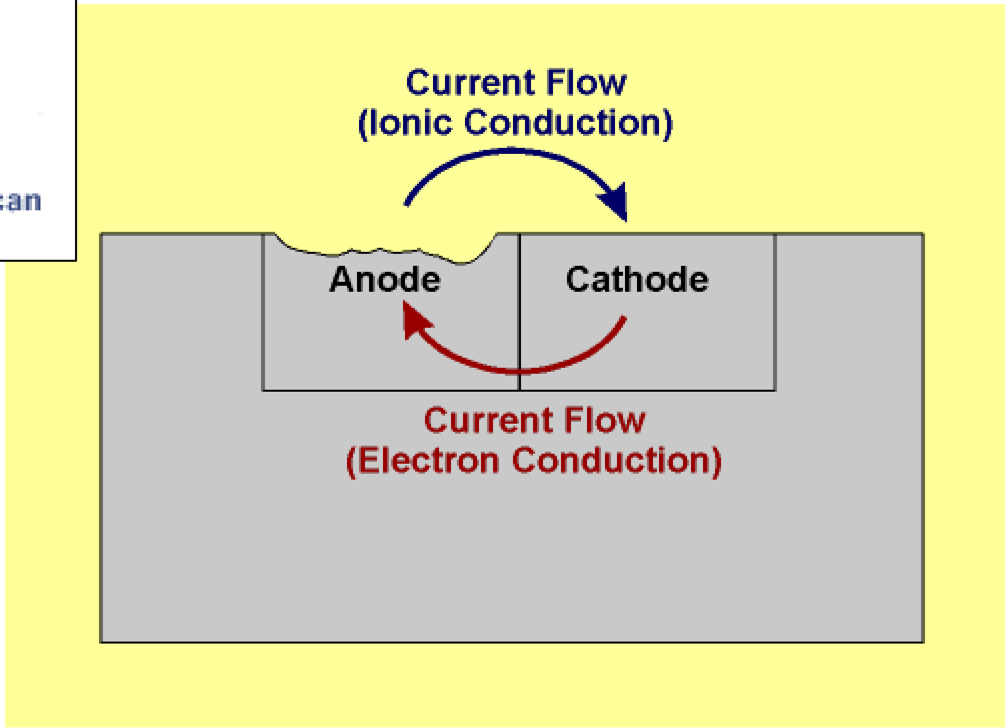


Platinum
Gold
Graphite
Titanium
Silver
316 Stainless Steel (passive)
Nickel (passive)
Copper
Nickel (active)
Tin
Lead
316 Stainless Steel (active)
Iron/Steel
Aluminum Alloys
Cadmium
Zinc
Magnesium

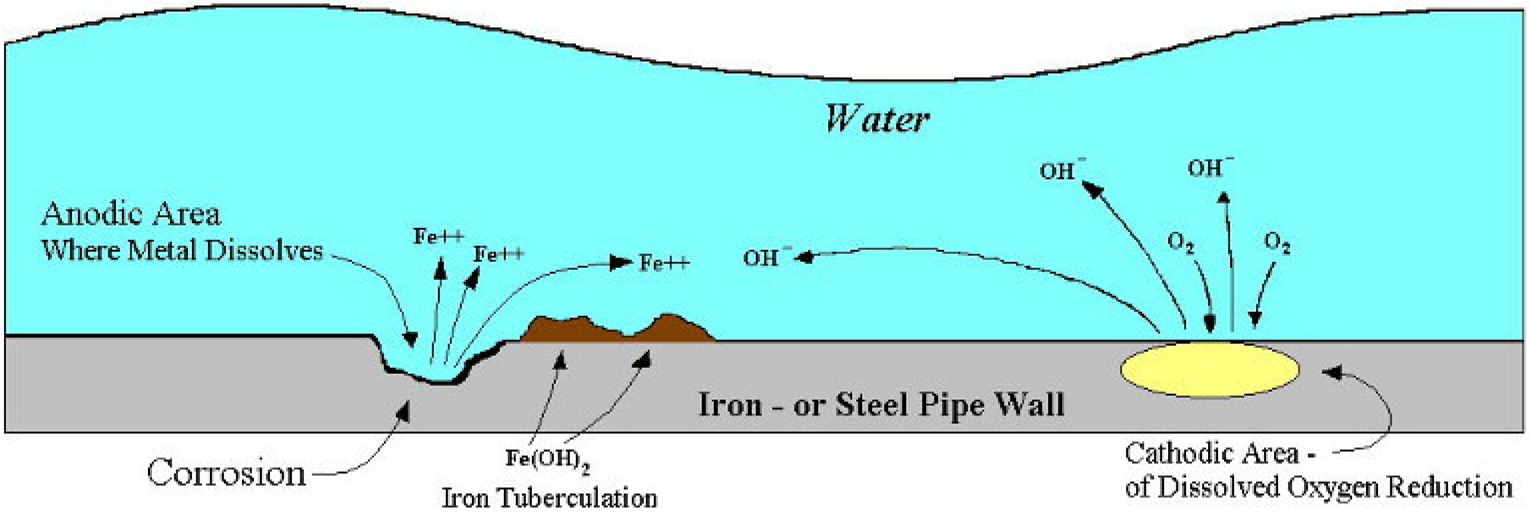
Table 18.2,
Callister
(Partial list)



A corrosion cell consists of four of elements and can exist in various sizes.



The Corrosion Cell :



Three Conditions are Known to Establish Corrosion Cells

1. Differences in composition.
2. Stress gradients and boundaries.
3. Concentration gradients

Composition Corrosion Cell

Composition cells, also known as ‘Galvanic cells’, arise when two metals with dissimilar compositions or microstructures come into contact in the presence of an electrolyte. The two most common examples follow:

1. Dissimilar metals: Formed by two single-phase metals in contact, such as iron and zinc, or nickel and gold. The metal that is higher on the Electrochemical Series will be the cathode. The other metal will suffer anodic reactions and will corrode.

2. Multi-phase alloy: Formed by a metal alloy composed of multiple phases, such as a stainless steel, a cast iron, or an aluminum alloy. The individual phases possess different electrode potentials, resulting in one phase acting as an anode and subject to corrosion.

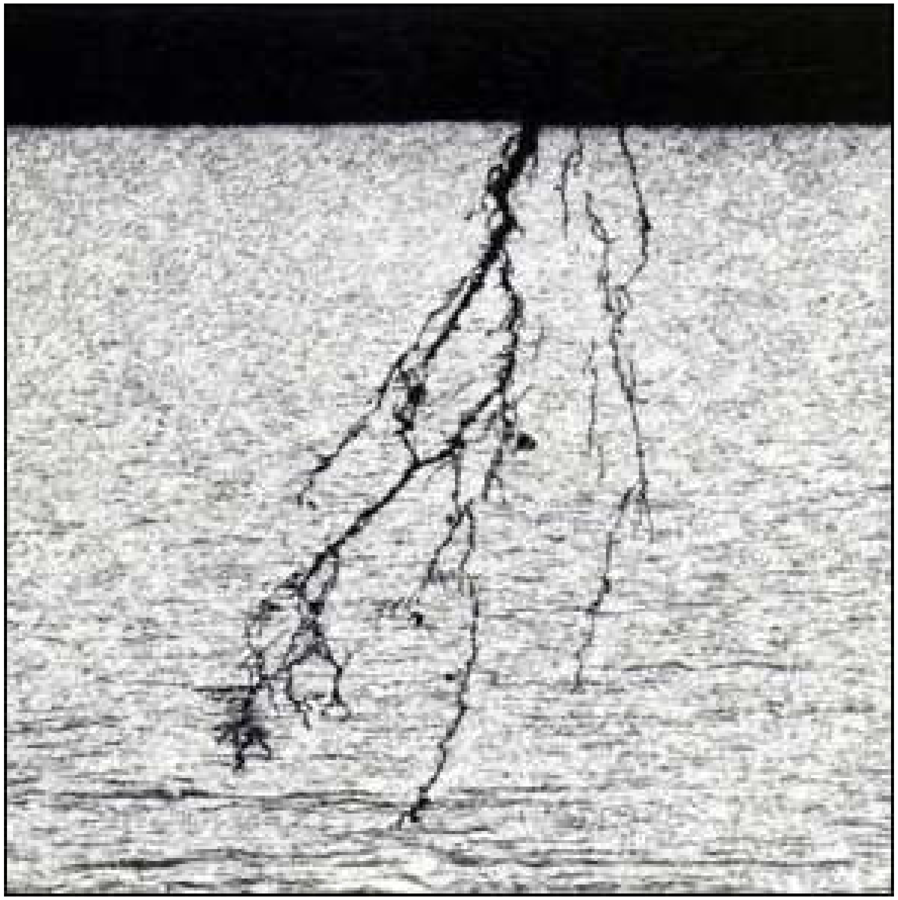
Stress Corrosion Cell

Stress cells can exist in a single piece of metal where a portion of the metal's microstructure possesses more stored strain energy than the rest of the metal. Metal atoms are at their lowest strain energy state when situated in a regular crystal array.

1. **Grain boundaries:** By definition, metal atoms situated along grain boundaries are not located in a regular crystal array (i.e. a grain). Their increased strain energy translates into an electrode potential that is anodic to the metal in the grains proper. Thus, corrosion can selectively occur along grain boundaries.

2. **High localized stress:** Regions within a metal subject to a high local stress will contain metal atoms at a higher strain energy state. As a result, high-stress regions will be anodic to low-stress regions and can corrode selectively. For example, bolts under load are subject to more corrosion than similar bolts that are unloaded.

3. **Cold worked:** Regions within a metal subjected to cold-work contain a higher concentration of dislocations, and as a result will be anodic to non-cold-worked regions. Thus, cold-worked sections of a metal will corrode faster. For example, nails that are bent will often corrode at the bend, or at their head where they were worked by the hammer.



Stress corrosion cracking is believed to be nucleated at pitting damage sites and develops under the action of local tensile stresses as a highly branched network of fine cracks. At each crack tip the combined action of the tensile stress and specific ions in the corrosive media cause continual crack propagation with little evidence of local deformation.

Concentration Corrosion Cell

Concentration cells can arise when the concentration of one of the species participating in a corrosion reaction varies within the electrolyte.

1. Electrolyte concentration: Consider a metal bathed in an electrolyte containing its own ions. The basic corrosion reaction where a metal atom losses an electron and enters the electrolyte as an ion can proceed both forward and backwards, and will eventually reach equilibrium. If a region of the electrolyte (adjacent to the metal) were to exhibit a decreased concentration of metal ions, this region would become anodic to the other portions of the metal surface. As a result, this portion of the metal would corrode faster in order to increase the local ion concentration.

2. Oxidation concentration: Perhaps the most common concentration cell affecting engineered structures is that of dissolve oxygen. When oxygen has access to a moist metal surface, corrosion is promoted. However, it is promoted the most where the oxygen concentration is the lowest. As a result, sections of a metal that are covered by dirt or scale will often corrode faster, since the flow of oxygen to these sections is restricted. An increased corrosion rate will lead to increased residue, further restricting the oxygen flow to worsen the situation. Pitting often results from this "runaway" reaction.

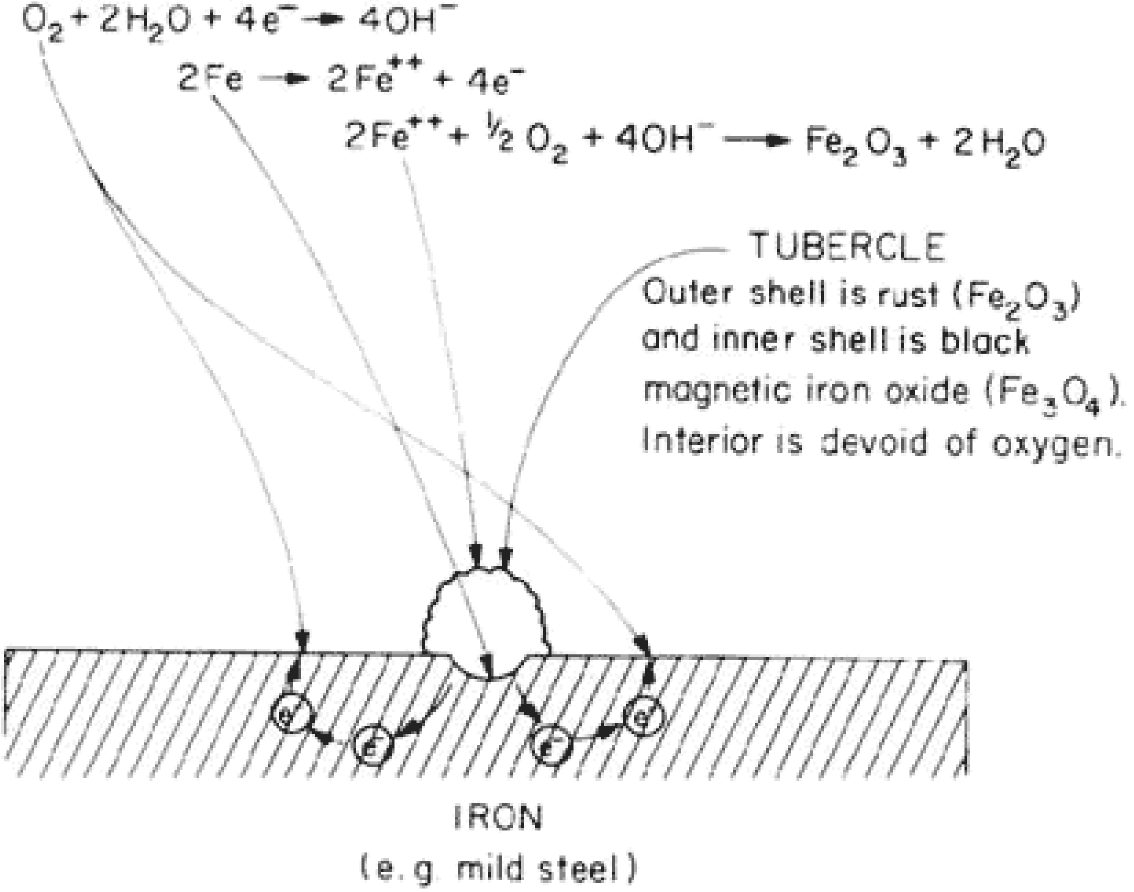


FIGURE 5. Oxygen Concentration Cell

Metal Alloys

While there are a large number of metals and alloys known, only a few have been considered for implant materials.

The performance of any material in the body will be controlled by two characteristics: biofunctionality and biocompatibility. The wide range of metals and alloys currently available allow material selections to be made to satisfy mechanical and physical functionality. However, the relatively corrosive environment of the body combined with the poor tolerance of the body for even minute concentrations of most metallic corrosion products eliminates most metallic materials. The selection of materials for medical devices is usually weighted towards considerations of “biocompatibility”.

Metal material properties can manipulated by mixing with other metals (or non-metals) to form alloys

An alloy is a combination, either in solution or compound, of two or more elements, which has a combination of at least two metals, and where the resultant material has metallic properties. An alloy with two components is called a binary alloy; one with three is a ternary alloy; one with four is a quaternary alloy. The result is a metallic substance with physical properties different from those of its components. Alloys are usually designed to have properties that are more desirable than those of their components. For instance, steel is stronger than iron, one of its main elements, and brass is more durable than copper, but more attractive than zinc.

There are three classes of metal alloys that are used in implant applications

1. Stainless steels
2. Cobalt chrome alloys
3. Titanium and titanium alloys

Stainless Steels

The austenitic stainless steels, especially Types 316 and 316L, are most widely used for implant fabrication. Stainless steel that has a low content of impurities and a passivated finish is entirely suitable for implantation in the human body. Forged stainless steel has a greater yield strength than cast stainless steels, but has a lower fatigue strength than other implant alloys. Stainless steel is no longer used routinely, from the standpoint of erosion, biocompatability, and fatigue life, stainless steel is inferior to other super alloys.

The only difference in composition between 316L and 316 stainless steel is the content of carbon. A wide range of properties exists depending on the heat treatment (annealing to obtain softer materials) or cold working (for greater strength and hardness). Even the 316L stainless steels may corrode inside the body under certain circumstances in a highly stressed and oxygen depleted region, such as contact under screws or fracture plates. Thus, stainless steels are suitable to use only in temporary implant devices, such as fractures plates, screws and hip nails.

New nickel-free stainless steels have been recently developed primarily to address the issue of nickel sensitivity. These stainless steels also have superior mechanical properties and better corrosion resistance.

Cobalt Chrome Alloys

There are basically two types of cobalt chromium alloys. One is the cobalt CoCrMo alloy, which is usually used to cast a product and the other is the CoNiCrMo alloy, which is usually wrought by (hot) forging. The castable CoCrMo alloy has been used for many decades in dentistry and recently, in making artificial joints. The wrought CoNiCrMo alloy is now used for making the stems of prosthesis for heavily loaded joints such as the knee and hip. Cobalt-based alloys are highly resistant to corrosion and especially to attack by chloride. As in all highly alloyed metals in the body environment, galvanic corrosion can occur, but to a lesser extent than in the iron-based alloys.

Cobalt-based alloys are quite resistant to fatigue and to cracking caused by corrosion, and they are not brittle, since they have a minimum of 8% elongation. However, as is true of other alloys, cobalt based alloys may fail because of fatigue fracture (but less often than stainless steel stems). The superior fatigue and ultimate tensile strength of the wrought CoNiCrMo alloy make it suitable for the applications which require long service without fracture or stress fatigue. Such is the case for the stems of the hip joint prosthesis. The modulus of elasticity values are higher than other materials such as stainless steels.

Titanium and Titanium-based Alloys

Attempts to use titanium for implant fabrication dates to the late 1930's. It was found that titanium was tolerated in cat femurs, as was stainless steel and vitalium (a CoCrMo alloy). Titanium's lightness and good mechanical and chemical properties are salient features for implant applications. One titanium alloy (Ti6Al4V) is widely used to manufacture implants. The main alloying elements of the alloy are aluminium (5.5 - 6.5%) and vanadium (3.5 - 4.5%). While the strength of the titanium alloys varies from lower than to equal to that of 316 stainless steel, when compared by specific strength (strength per density), the titanium alloys out perform any other implant material. Titanium nevertheless, has poor shear strength, making it less desirable for bone screws, plates and similar applications.

Titanium also tends to seize when in sliding contact with itself or other metal. Titanium-based alloys that have a high coefficient of friction which can cause problems. Wear particles are formed in a piece of bone if a piece of bone rubs against the implant, or if two parts of an implant rub against one another. Therefore, implants of titanium-on-titanium generally are not used as joint surfaces. Titanium derives its corrosion resistance to the formation of a surface oxide film. Under in vivo conditions, the oxide is the only stable reaction product.

Solid Solution Alloys

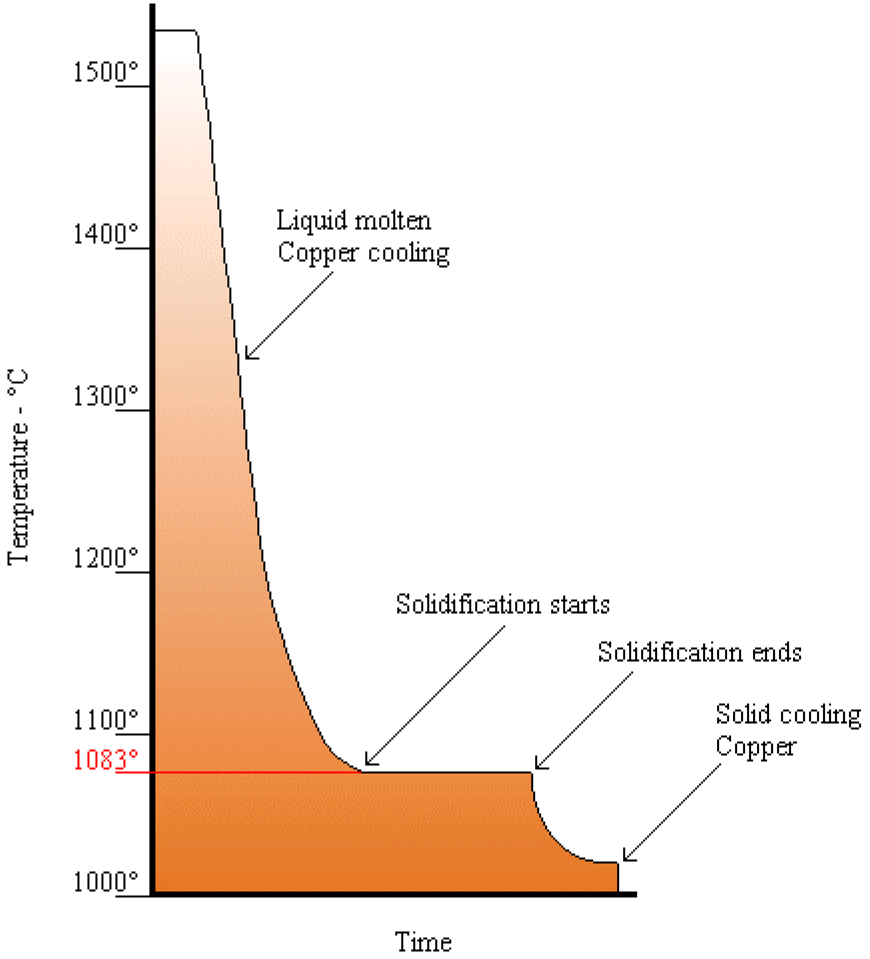
A solid solution alloy is a miscible blend of two metallic elements. The “solvent” or major component forms the parent crystal structure lattice, which is not substantially altered by the presence of the “solute(s)” or minor component(s). There are two types of solutions alloys;

1. Substitutional solid solution

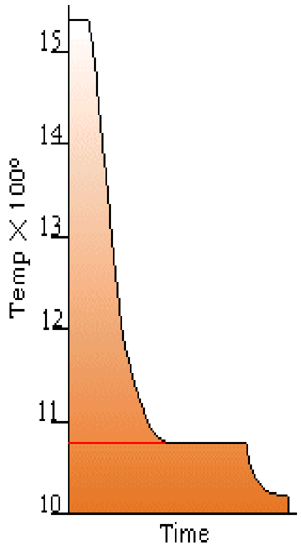
2. Interstitial solid solution

Under the microscope, the alloy will appear as a pure metal. The impact on lattice potentials usually results in stronger, harder, less ductile metal.

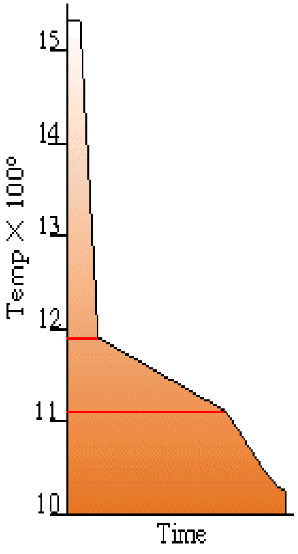
The formations of alloys occurs from the cooling of molten metal solutions.



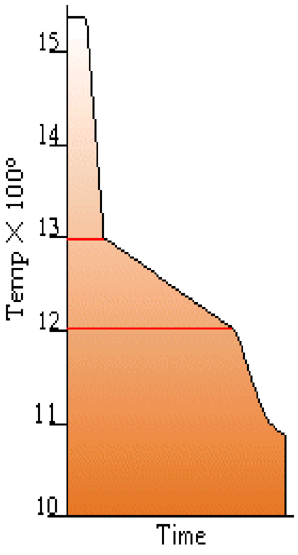
When copper cools from the molten state to 1083℃, dramatic change takes place. The copper starts to solidify. As it solidifies, there is no drop in temperature. The points of importance to an engineer on a cooling curve diagram are the temperatures at which Solidification Starts and Solidification Ends. For a pure metal the temperature for both is the same.



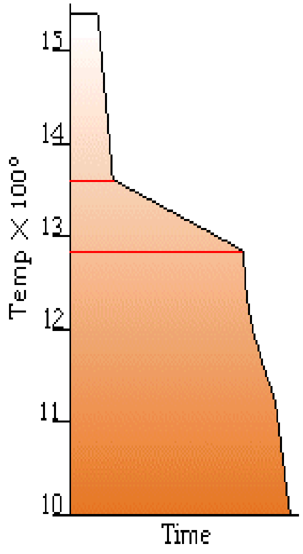
100% Copper



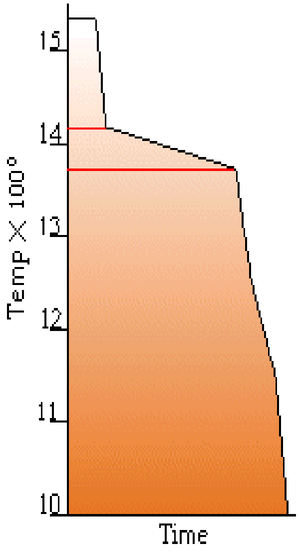
80% Copper - 20% Nickel



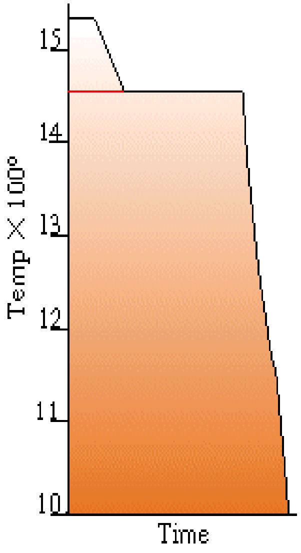
60% Copper - 40% Nickel



40% Copper - 60% Nickel

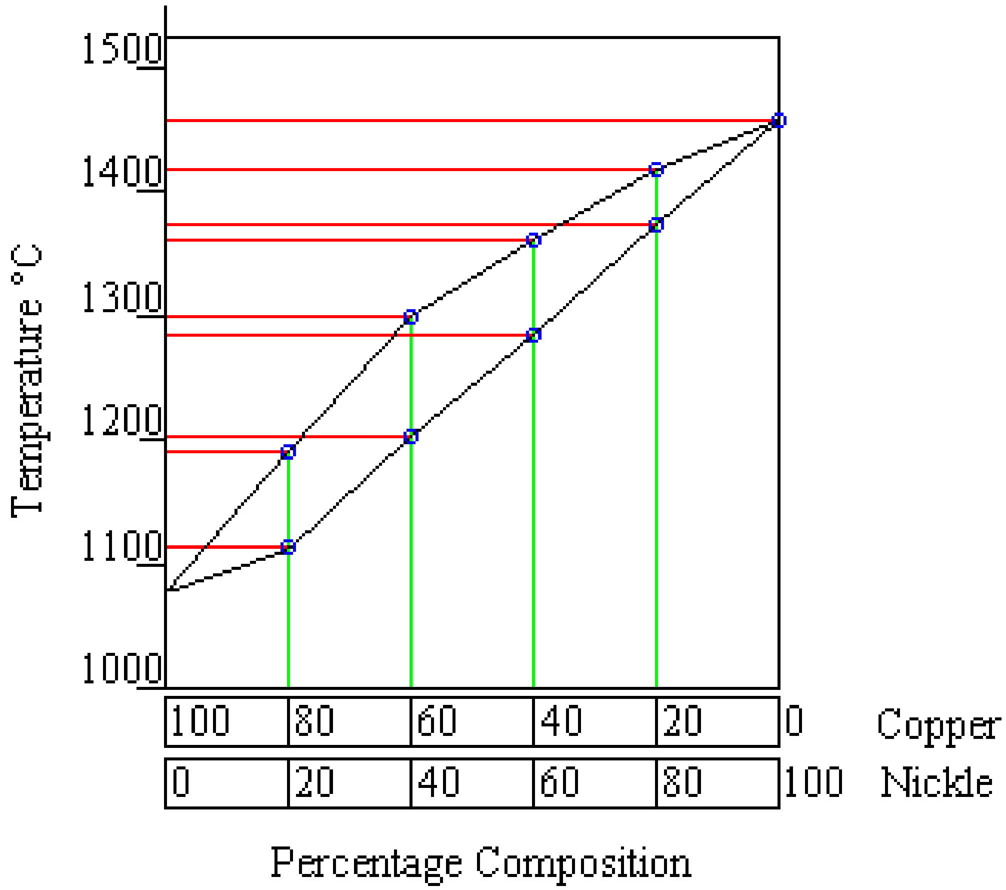


20% Copper - 80% Nickel



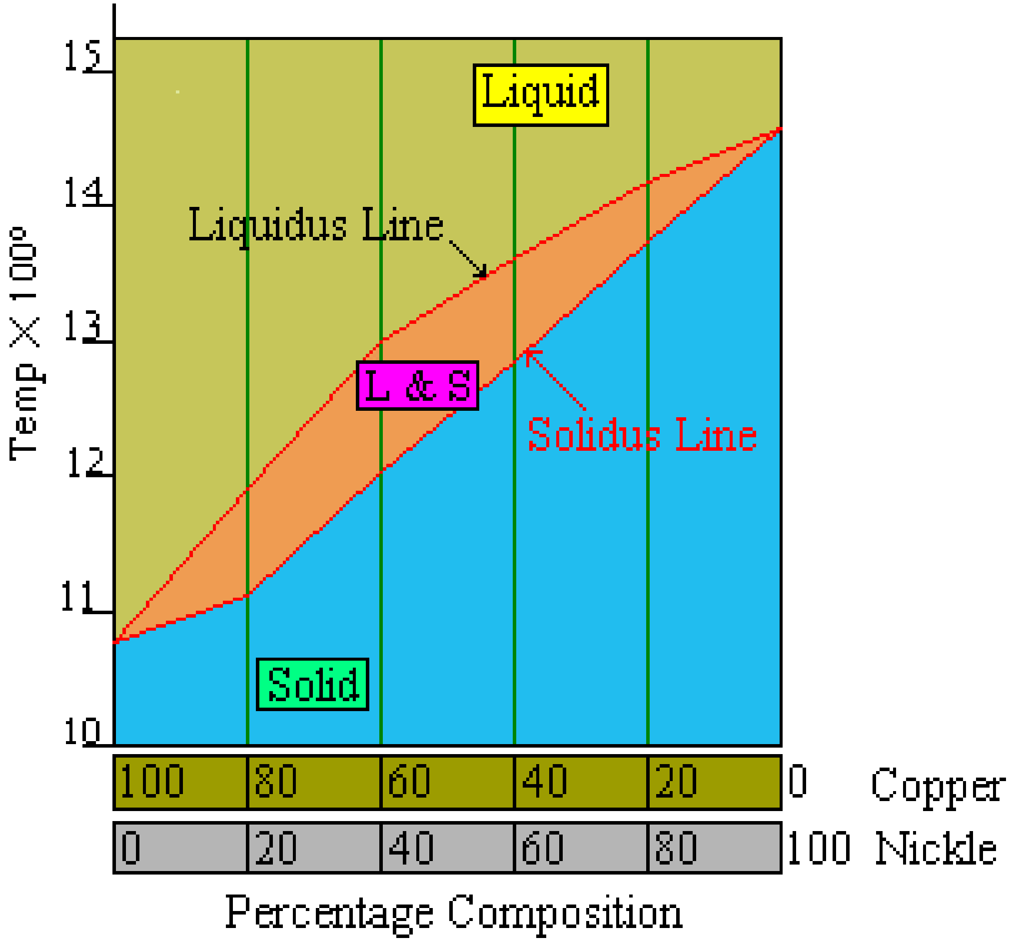
100% Nickel

Firstly a cooling curve is developed for each of the different alloy compositions. The temperatures at which solidification starts and solidification ends are noted. This information is then transferred to a single graph where all of the different compositions can be shown together. It is important to notice on the cooling curves of the alloys, that as they solidify there is a drop in temperature. For pure metals there is no change in temperature.



On this phase diagram there are 2 important lines and 3 important areas. The liquidus line, which joins the solidification start points on the diagram, indicates that above the line the alloys are liquid. The solidus indicates that below the line the alloys are solid.

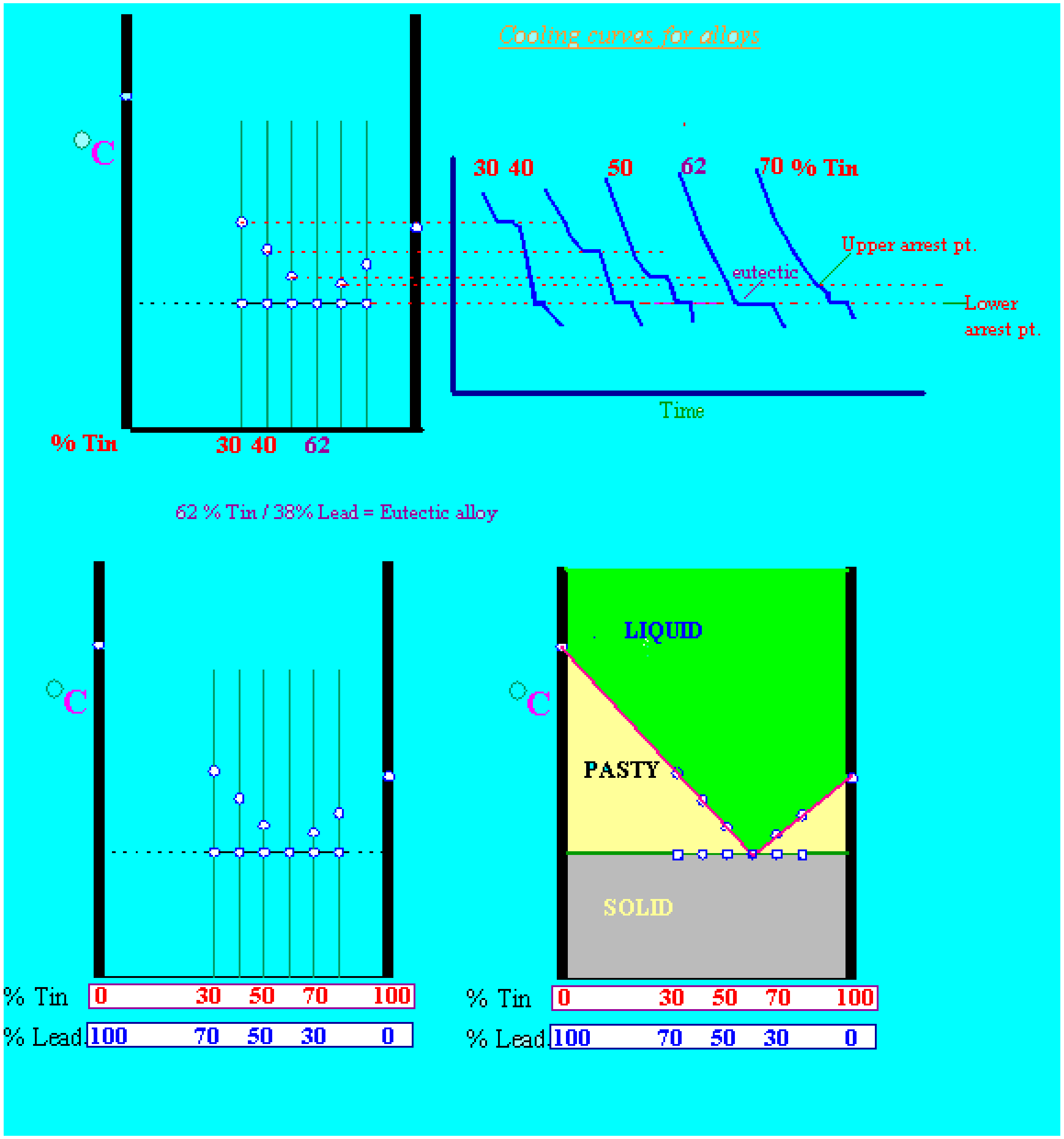
In between the liquidus line and the solidus line the alloys are a heterogeneous mixture of solid and liquid.



Solid Mixtures

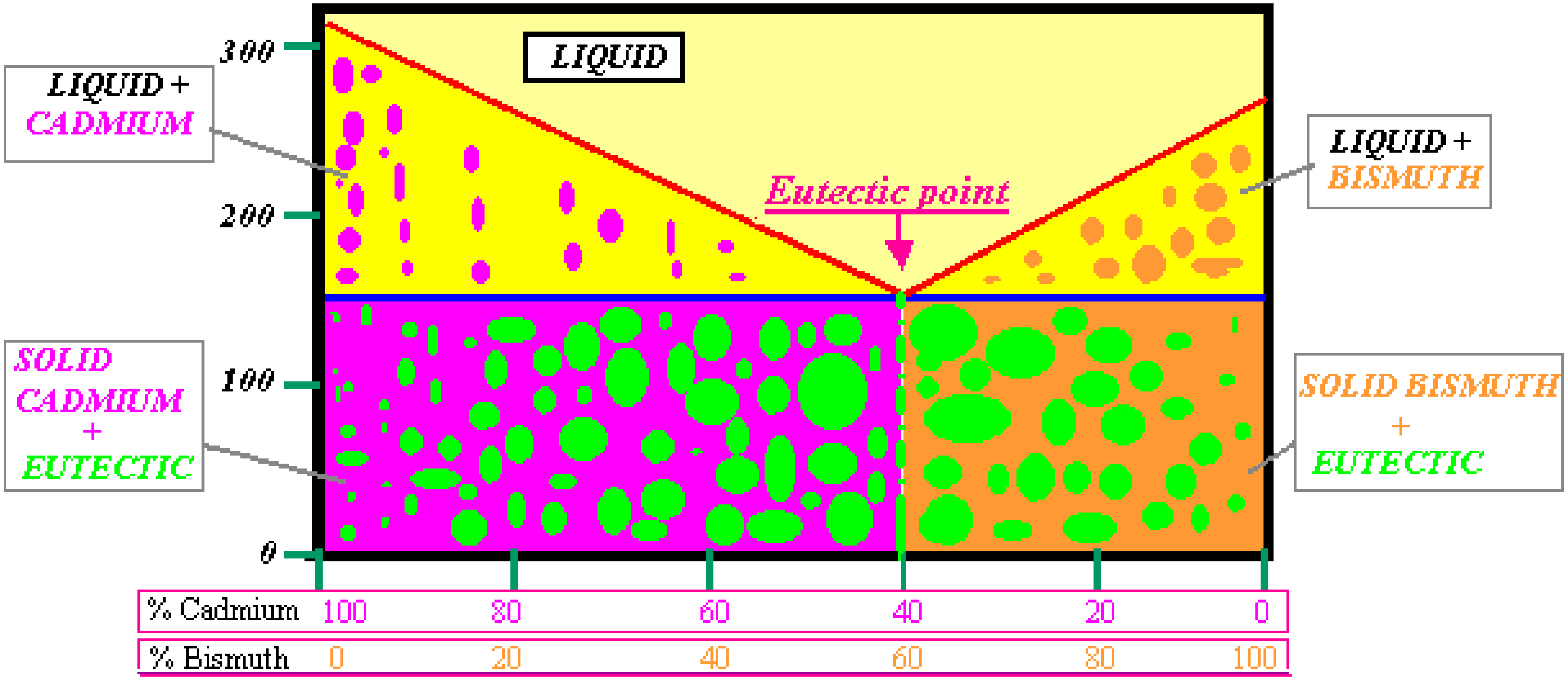
A Eutectic equilibrium diagram results when the two metals are soluble in the liquid state but insoluble in the solid state. On cooling the liquid condenses to a constant melting mixture. The grain of the solid alloy consist of two distinguishable metal phases which can be seen under a microscope to be like a layer of one metal on top of a layer of the other metal.

The proper ratios of components to obtain a eutectic alloy is identified by the eutectic point on a phase diagram. The term comes from the Greek 'eutektos', meaning 'easily melted.'



http://www.ul.ie/~walshem/fyp/solid%20solution1.htm#Eutectic%20thermal%20equilibrium

Understanding the Eutectic thermal equilibrium diagram



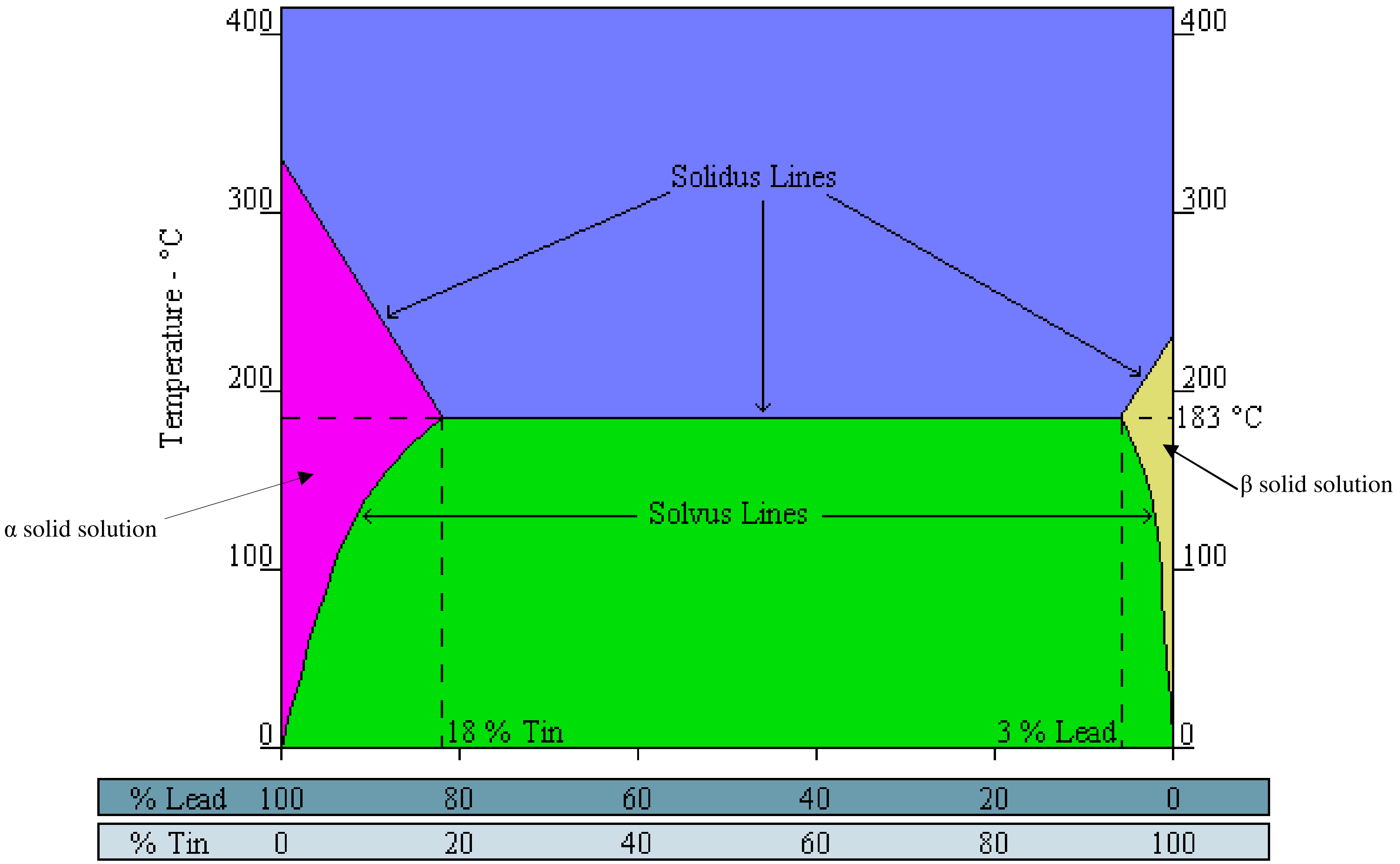
This phase diagram differs from the solid solution diagram. The main difference is caused by the eutectic point. Here the alloy changes straight from a liquid to a solid without going through the “pasty phase”. It should also be noted that the melting temperature of this alloy is well below the melting temperature of either of the two metals on their own. As usual above the liquidus line the alloy is totally liquid, and the two metals are totally soluble in one another. The solid area can be broken up into 3 sections. Below the eutectic point the solid is a eutectic grain mixture, (i.e. alternating layers of each metal). To either side of the eutectic point the solid is in the form of grains of one of the metals embedded in solid eutectic.

http://www.ul.ie/~walshem/fyp/Eutectic%20alloys.htm

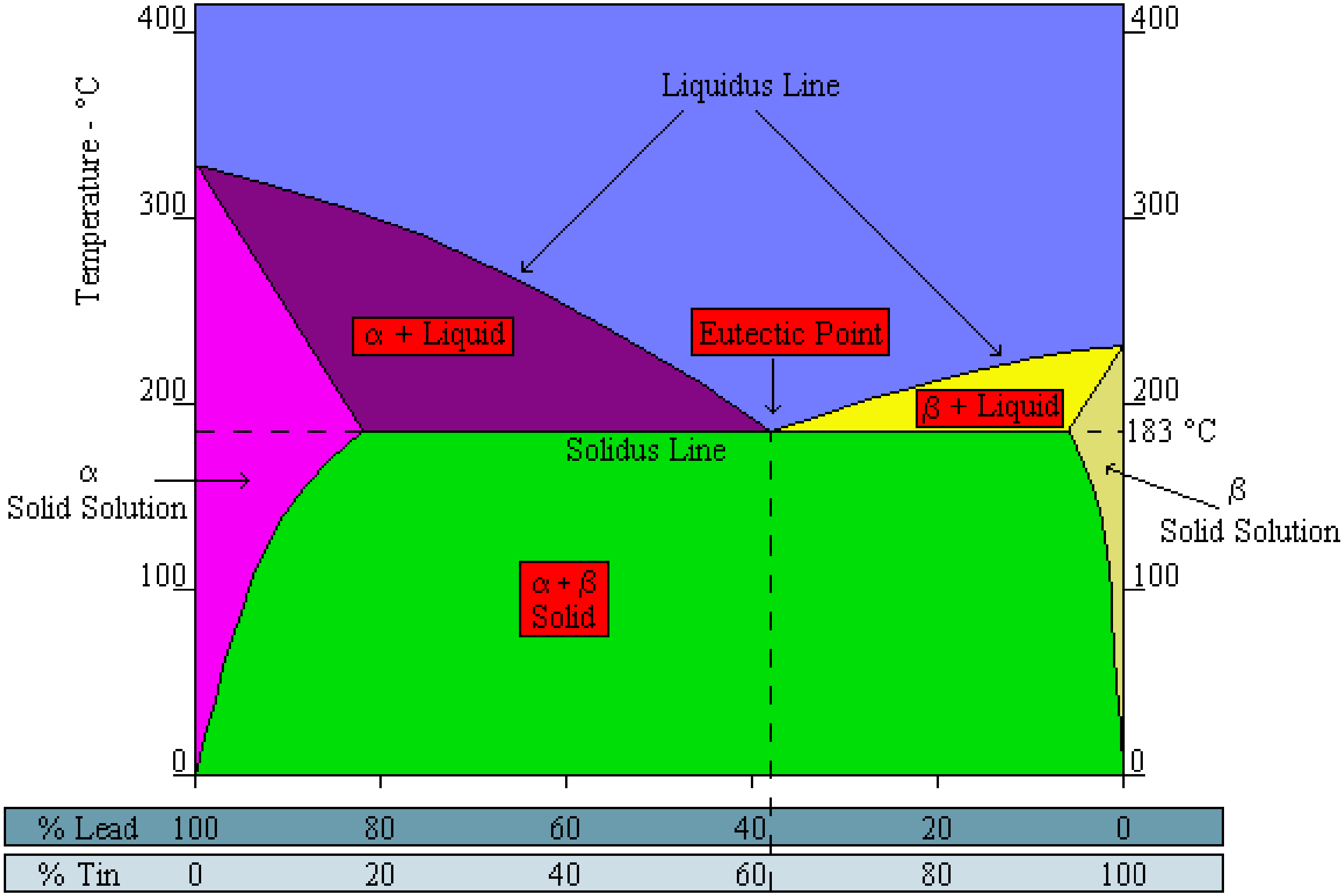
A “phase” is a distinct state of matter in a system; matter that is identical in chemical composition and physical state and separated from other material by the phase boundary.

A solid solution forms a single solid phase because it is miscible in all proportions. Not all metal mixtures form a single phase.

A partial solubility alloy can have a complex phase diagram. Metals that alloy is this manner have composition regions where solid solutions will form and regions where eutectics will form. Their phase diagram has elements which combines features of solid solution alloy and a eutectic alloy.

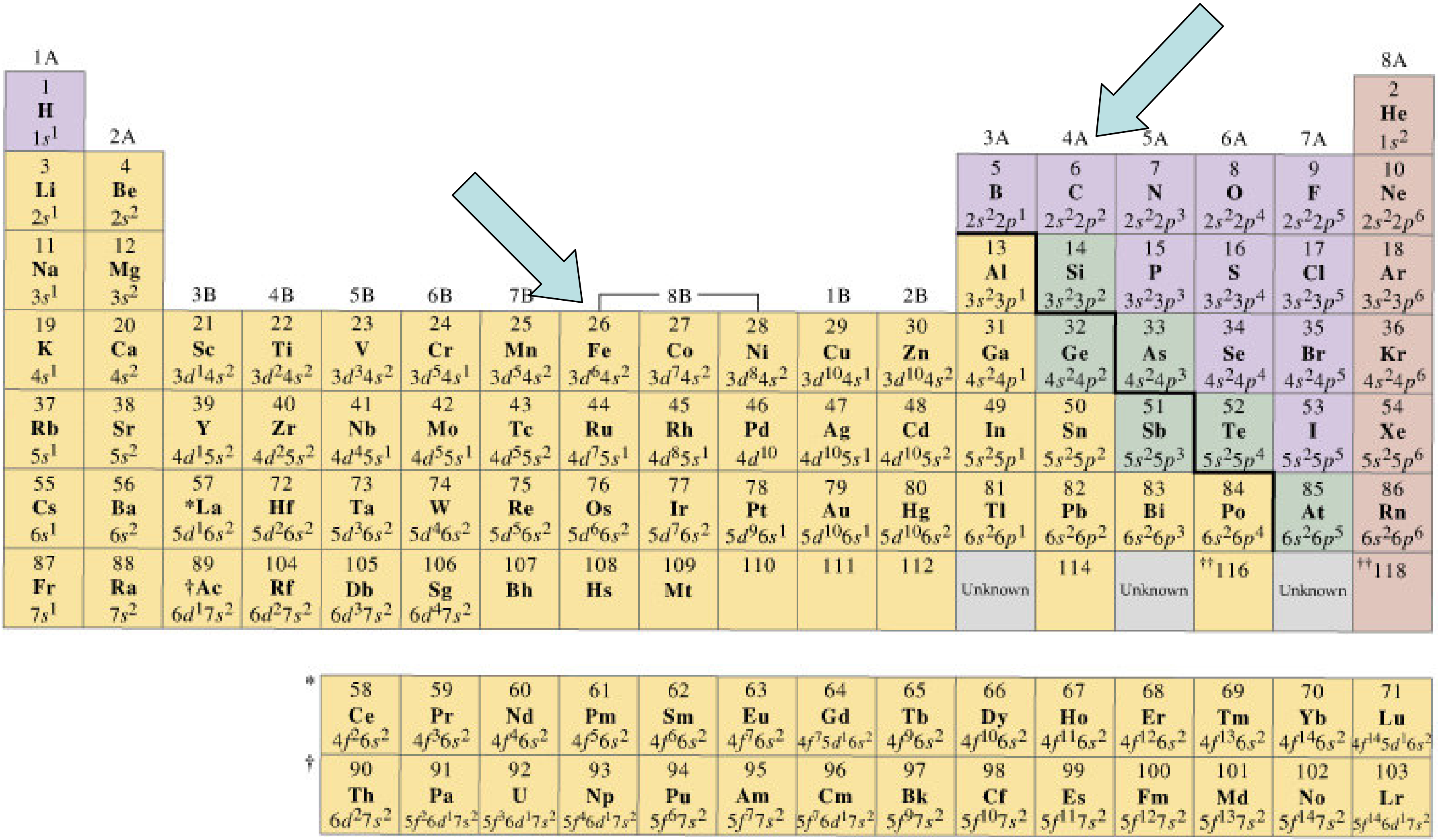


The solid solution component of the phase diagram shows two regions at the composition extremes where solid solutions form. At 183℃, 18% Sn can be dissolved in Pb, and 3% Pb can be dissolved in Sn. On the left between the solidus line and the solvus line we have α, (alpha) metal, a solid solution alloy of lead and tin. On the right between the solidus line and the solvus line we have β, (beta) metal, another solid solution of lead and tin. In between the two solvus lines and the solidus line we have a eutectic mixture of lead and tin.



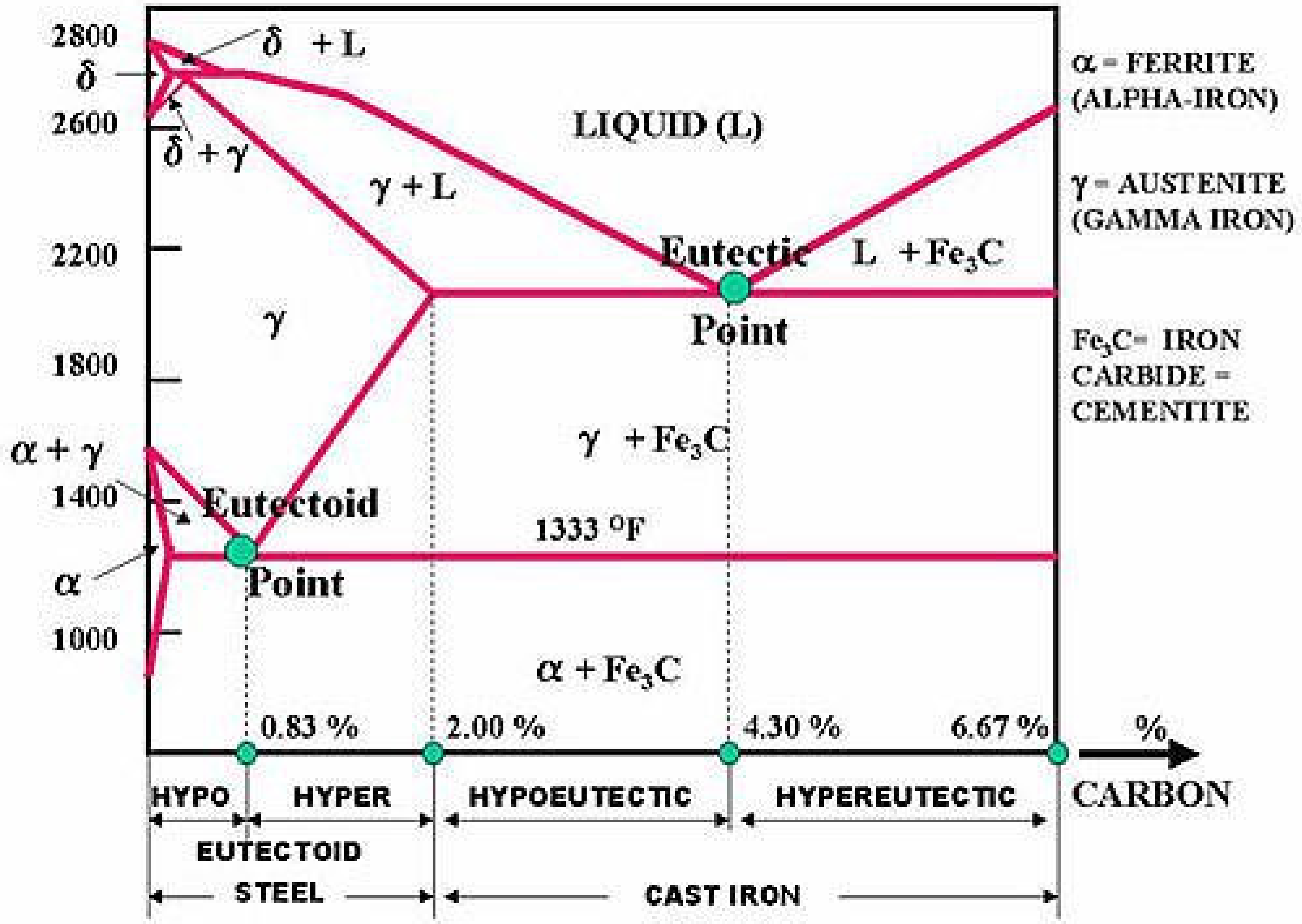
The eutectic component completes the partial solubility diagram. Again we have a eutectic point present, where the alloy changes from a liquid to a solid without going through the "pasty" stage. The "pasty" areas comprise of alpha, (the first), metal and liquid, to the left of the Eutectic Point, and beta, (the second), metal and liquid to the right.

Periodic Chart of the Elements



1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
1 **H** $1s^1$																	2 **He** $1s^2$
3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^2 2p^1$	6 **C** $2s^2 2p^2$	7 **N** $2s^2 2p^3$	8 **O** $2s^2 2p^4$	9 **F** $2s^2 2p^5$	10 **Ne** $2s^2 2p^6$
11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^2 3p^1$	14 **Si** $3s^2 3p^2$	15 **P** $3s^2 3p^3$	16 **S** $3s^2 3p^4$	17 **Cl** $3s^2 3p^5$	18 **Ar** $3s^2 3p^6$
19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^1 4s^2$	22 **Ti** $3d^2 4s^2$	23 **V** $3d^3 4s^2$	24 **Cr** $3d^5 4s^1$	25 **Mn** $3d^5 4s^2$	26 **Fe** $3d^6 4s^2$	27 **Co** $3d^7 4s^2$	28 **Ni** $3d^8 4s^2$	29 **Cu** $3d^{10} 4s^1$	30 **Zn** $3d^{10} 4s^2$	31 **Ga** $4s^2 4p^1$	32 **Ge** $4s^2 4p^2$	33 **As** $4s^2 4p^3$	34 **Se** $4s^2 4p^4$	35 **Br** $4s^2 4p^5$	36 **Kr** $4s^2 4p^6$
37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^1 5s^2$	40 **Zr** $4d^2 5s^2$	41 **Nb** $4d^4 5s^1$	42 **Mo** $4d^5 5s^1$	43 **Tc** $4d^5 5s^2$	44 **Ru** $4d^7 5s^1$	45 **Rh** $4d^8 5s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10} 5s^1$	48 **Cd** $4d^{10} 5s^2$	49 **In** $5s^2 5p^1$	50 **Sn** $5s^2 5p^2$	51 **Sb** $5s^2 5p^3$	52 **Te** $5s^2 5p^4$	53 **I** $5s^2 5p^5$	54 **Xe** $5s^2 5p^6$
55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 ***La** $5d^1 6s^2$	72 **Hf** $5d^2 6s^2$	73 **Ta** $5d^3 6s^2$	74 **W** $5d^4 6s^2$	75 **Re** $5d^5 6s^2$	76 **Os** $5d^6 6s^2$	77 **Ir** $5d^7 6s^2$	78 **Pt** $5d^9 6s^1$	79 **Au** $5d^{10} 6s^1$	80 **Hg** $5d^{10} 6s^2$	81 **Tl** $6s^2 6p^1$	82 **Pb** $6s^2 6p^2$	83 **Bi** $6s^2 6p^3$	84 **Po** $6s^2 6p^4$	85 **At** $6s^2 6p^5$	86 **Rn** $6s^2 6p^6$
87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **†Ac** $6d^1 7s^2$	104 **Rf** $6d^2 7s^2$	105 **Db** $6d^3 7s^2$	106 **Sg** $6d^4 7s^2$	107 **Bh**	108 **Hs**	109 **Mt**	110	111	112	Unknown	114	Unknown	††116	Unknown	††118

*	58 **Ce** $4f^2 6s^2$	59 **Pr** $4f^3 6s^2$	60 **Nd** $4f^4 6s^2$	61 **Pm** $4f^5 6s^2$	62 **Sm** $4f^6 6s^2$	63 **Eu** $4f^7 6s^2$	64 **Gd** $4f^7 5d^1 6s^2$	65 **Tb** $4f^9 6s^2$	66 **Dy** $4f^{10} 6s^2$	67 **Ho** $4f^{11} 6s^2$	68 **Er** $4f^{12} 6s^2$	69 **Tm** $4f^{13} 6s^2$	70 **Yb** $4f^{14} 6s^2$	71 **Lu** $4f^{14} 5d^1 6s^2$
†	90 **Th** $6d^2 7s^2$	91 **Pa** $5f^2 6d^1 7s^2$	92 **U** $5f^3 6d^1 7s^2$	93 **Np** $5f^4 6d^1 7s^2$	94 **Pu** $5f^6 7s^2$	95 **Am** $5f^7 7s^2$	96 **Cm** $5f^7 6d^1 7s^2$	97 **Bk** $5f^9 7s^2$	98 **Cf** $5f^{10} 7s^2$	99 **Es** $5f^{11} 7s^2$	100 **Fm** $5f^{12} 7s^2$	101 **Md** $5f^{13} 7s^2$	102 **No** $5f^{14} 7s^2$	103 **Lr** $5f^{14} 6d^1 7s^2$


2800
δ
2600
2200
1800
1400
1000
δ + L
δ + γ
LIQUID (L)
γ + L
γ
Eutectic
Point
L + Fe$_3$C
γ + Fe$_3$C
α + γ
Eutectoid
Point
1333 °F
α
α + Fe$_3$C
0.83 %
2.00 %
4.30 %
6.67 %
%
CARBON
HYPO
HYPER
EUTECTOID
HYPOEUTECTIC
HYPEREUTECTIC
STEEL
CAST IRON
α = FERRITE (ALPHA-IRON)
γ = AUSTENITE (GAMMA IRON)
Fe$_3$C = IRON CARBIDE = CEMENTITE

Historical Trivia

Harry Brearley, born in Sheffield, England, in 1871, probably invented stainless steel. His father was a steel smelter and through private study and night school he became an expert in the analysis of steel and its production. In 1908 Brearley was given the opportunity to set up the Brown Firth Laboratories. In 1912 Brearley was asked to help solve a problem of small arms barrel erosion. Brearley was therefore looking for a steel with better resistance to erosion, not corrosion. As a line of investigation he decided to experiment with steels containing chromium, as these were known to have a higher melting point than ordinary steels.

The first true stainless steel was melted on the 13th August 1913. It contained 0.24% carbon and 12.8% chromium. In order to examine the grain structure of the steel he needed to etch (attack with acid) samples before examining them under the microscope. The etching re-agents he used were nitric acid, vinegar and other food acids such as lemon juice. He found that this alloy resisted corrosion. Brearley immediately saw how this new steel could revolutionize the cutlery industry. On his own initiative, he then had knives made at a local cutler's, R.F. Mosley. It was Ernest Stuart, the cutlery manager of Mosley's who first referred to the new knives as "stainless" after, in experiments, he had failed to stain them with vinegar.

Stainless Steel

Alloying elements have significant effect on the iron-iron carbide equilibrium diagram. The addition of some of these alloying elements will widen the temperature range through which austenite (γ -iron) is stable while other elements will constrict the temperature range. What this means is that some elements will raise and some elements will lower the critical temperature of steel. Manganese, cobalt, and nickel increase the temperature range through which austenite is stable.

Stainless steel is defined as a ferrous alloy with a minimum of 10.5% chromium content. The name originates from the fact that stainless steel stains, or rusts, less easily than ordinary steel. Stainless steel has higher resistance to oxidation and corrosion in several environments.

High oxidation resistance in air at ambient temperature is normally achieved with additions of more than 12% (by weight) chromium. The chromium forms a layer of chromium (III) oxide (Cr2O3) when exposed to oxygen. The layer is too thin to be visible, meaning the metal stays shiny. It is, however, impervious to water and air, protecting the metal beneath. Also, when the surface is scratched this layer quickly reforms. This phenomenon is called passivation.

Passivation

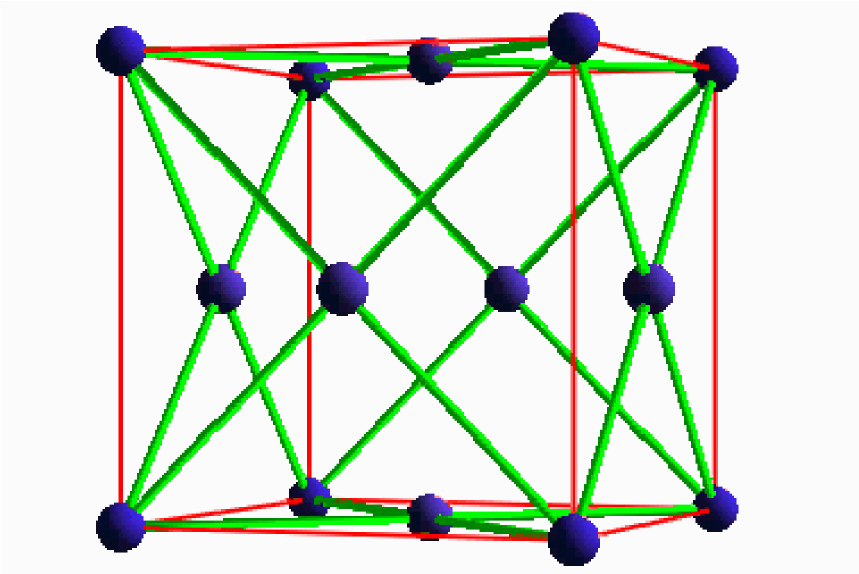
High oxidation resistance in air at ambient temperature is normally achieved with additions of more than 12% (by weight) chromium. The chromium in the steel combines with oxygen in the atmosphere to form a thin, invisible layer of chrome-containing oxide, called the passive film. The chromium forms a layer of chromium (III) oxide (Cr2O3) when exposed to oxygen. The sizes of chromium atoms and their oxides are similar, so they pack neatly together on the surface of the metal, forming a stable layer only a few atoms thick. The layer is too thin to be visible, meaning the metal stays shiny. It is, however, impervious to water and air, protecting the metal beneath.

If the metal is cut or scratched and the passive film is disrupted, more oxide will quickly form and recover the exposed surface, protecting it from oxidative corrosion. (Iron, on the other hand, rusts quickly because atomic iron is much smaller than its oxide, so the oxide forms a loose rather than tightly-packed layer and flakes away.) The passive film requires oxygen to self-repair, so stainless steels have poor corrosion resistance in low-oxygen and poor circulation environments. In seawater, chlorides from the salt will attack and destroy the passive film more quickly than it can be repaired in a low oxygen environment.

Question..?

If austenitic steel (γ-iron, fcc) is stable above about 1200℃, how can it be used at room temperature?

Austenitic – Face Centered Cubic (fcc)



Role of Alloying Elements

A property of great importance is the ability of alloying elements to promote the formation of a certain phase or to stabilize it. These elements are grouped as austenite-forming, ferrite-forming, carbide-forming and nitride-forming elements.

Austenite-forming elements

The elements C, Ni and Mn are important in stabilizing the fcc phase. Sufficiently large amounts of Ni or Mn render a steel austenitic even at room temperature. An example of this is the so-called Hadfield steel which contains 13% Mn, 12% Cr and l% C. In this steel both the Mn and C take part in stabilizing the austenite. Another example is austenitic stainless steel containing 18% Cr and 8% Ni.

Types of Stainless Steel

Austenitic

Austenitic steels have austenite as their primary phase (face centered cubic crystal). These are alloys containing chromium and nickel (sometimes manganese and nitrogen), structured around the Type 302 composition of iron, 18% chromium, and 8% nickel. Austenitic steels are not hardenable by heat treatment. The most familiar stainless steel is probably Type 304, sometimes called T304 or simply 304. Type 304 surgical stainless steel is an austenitic steel containing 18-20% chromium and 8-10% nickel.

Ferritic

Ferritic steels have ferrite (body centered cubic crystal) as their main phase. These steels contain iron and chromium, based on the Type 430 composition of 17% chromium. Ferritic steel is less ductile than austenitic steel and is not hardenable by heat treatment.

Martensitic

The characteristic orthorhombic martensite microstructure was first observed by German microscopist Adolf Martens around 1890. Martensitic steels are low carbon steels built around the Type 410 composition of iron, 12% chromium, and 0.12% carbon. They may be tempered and hardened. Martensite gives steel great hardness, but it also reduces its toughness and makes it brittle, so few steels are fully hardened.

Table 1. Composition ranges for 316 grade of stainless steels.

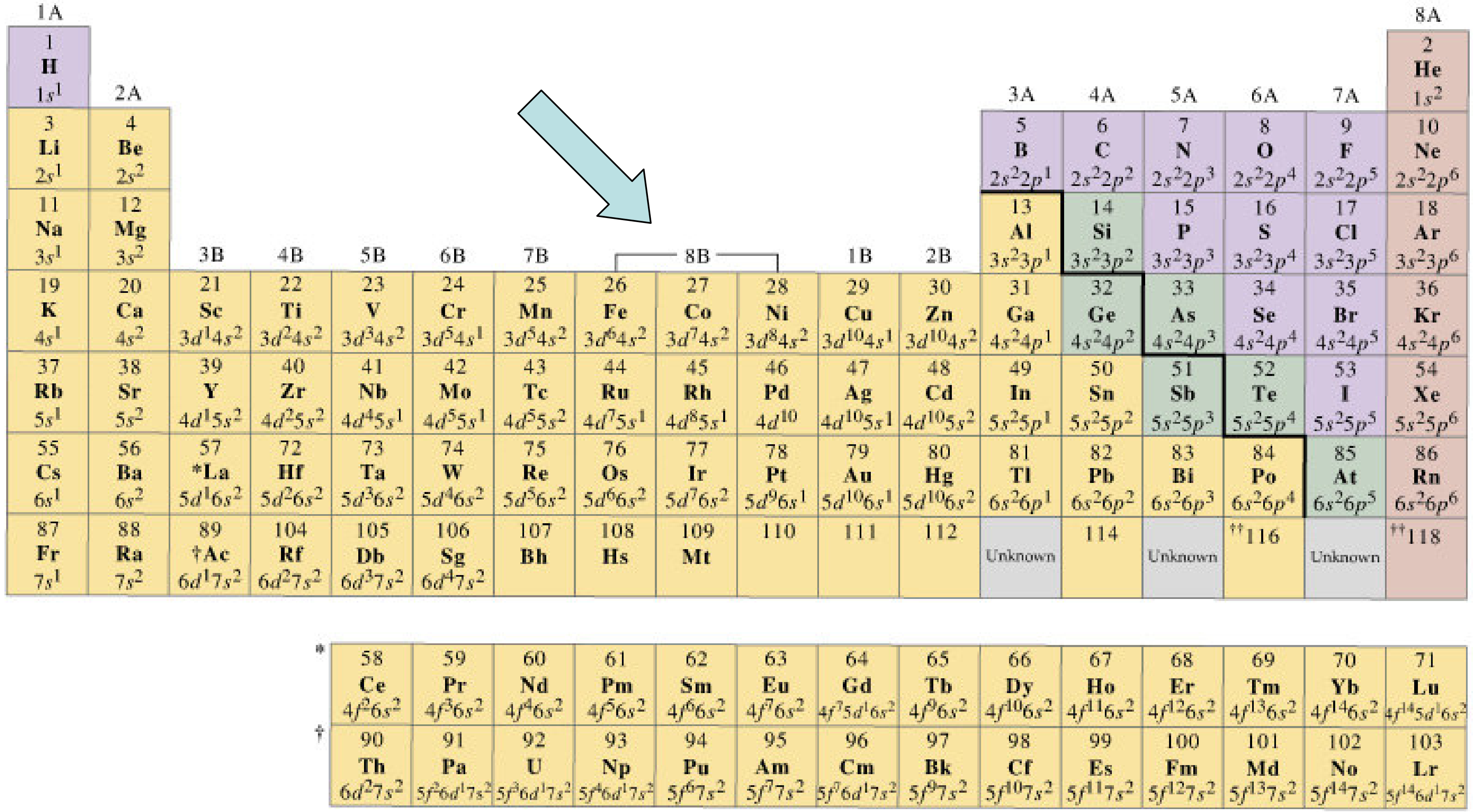
Grade		C	Mn	Si	P	S	Cr	Mo	Ni	N
316	Min	-	-	-	0	-	16.0	2.00	10.0	-
	Max	0.08	2.0	0.75	0.045	0.03	18.0	3.00	14.0	0.10
316L	Min	-	-	-	-	-	16.0	2.00	10.0	-
	Max	0.03	2.0	0.75	0.045	0.03	18.0	3.00	14.0	0.10
316H	Min	0.04	0.04	0	-	-	16.0	2.00	10.0	-
	max	0.10	0.10	0.75	0.045	0.03	18.0	3.00	14.0	-

Table 2. Mechanical properties of 316 grade stainless steels.

Grade	Tensile Str (MPa) min	Yield Str 0.2% Proof (MPa) min	Elong (% in 50mm) min	Hardness	
				Rockwell B (HR B) max	Brinell (HB) max
316	515	205	40	95	217
316L	485	170	40	95	217
316H	515	205	40	95	217

Note: 316H also has a requirement for a grain size of ASTM no. 7 or coarser.

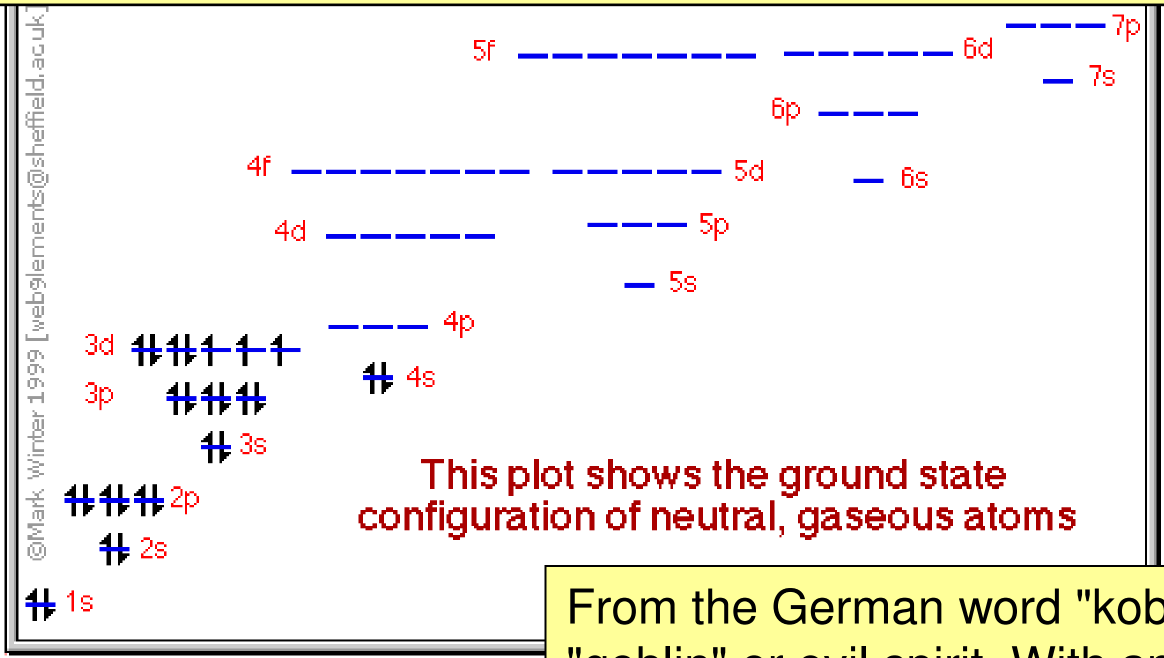
Periodic Chart of the Elements



1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
1 **H** $1s^1$																	2 **He** $1s^2$
3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	31 **Ga** $4s^24p^1$	32 **Ge** $4s^24p^2$	33 **As** $4s^24p^3$	34 **Se** $4s^24p^4$	35 **Br** $4s^24p^5$	36 **Kr** $4s^24p^6$
37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^45s^1$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	49 **In** $5s^25p^1$	50 **Sn** $5s^25p^2$	51 **Sb** $5s^25p^3$	52 **Te** $5s^25p^4$	53 **I** $5s^25p^5$	54 **Xe** $5s^25p^6$
55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 ***La** $5d^16s^2$	72 **Hf** $5d^26s^2$	73 **Ta** $5d^36s^2$	74 **W** $5d^46s^2$	75 **Re** $5d^56s^2$	76 **Os** $5d^66s^2$	77 **Ir** $5d^76s^2$	78 **Pt** $5d^96s^1$	79 **Au** $5d^{10}6s^1$	80 **Hg** $5d^{10}6s^2$	81 **Tl** $6s^26p^1$	82 **Pb** $6s^26p^2$	83 **Bi** $6s^26p^3$	84 **Po** $6s^26p^4$	85 **At** $6s^26p^5$	86 **Rn** $6s^26p^6$
87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **†Ac** $6d^17s^2$	104 **Rf** $6d^27s^2$	105 **Db** $6d^37s^2$	106 **Sg** $6d^47s^2$	107 **Bh**	108 **Hs**	109 **Mt**	110	111	112	Unknown	114	Unknown	††116	Unknown	††118

*	58 **Ce** $4f^26s^2$	59 **Pr** $4f^36s^2$	60 **Nd** $4f^46s^2$	61 **Pm** $4f^56s^2$	62 **Sm** $4f^66s^2$	63 **Eu** $4f^76s^2$	64 **Gd** $4f^75d^16s^2$	65 **Tb** $4f^96s^2$	66 **Dy** $4f^{10}6s^2$	67 **Ho** $4f^{11}6s^2$	68 **Er** $4f^{12}6s^2$	69 **Tm** $4f^{13}6s^2$	70 **Yb** $4f^{14}6s^2$	71 **Lu** $4f^{14}5d^16s^2$
†	90 **Th** $6d^27s^2$	91 **Pa** $5f^26d^17s^2$	92 **U** $5f^36d^17s^2$	93 **Np** $5f^46d^17s^2$	94 **Pu** $5f^67s^2$	95 **Am** $5f^77s^2$	96 **Cm** $5f^76d^17s^2$	97 **Bk** $5f^97s^2$	98 **Cf** $5f^{10}7s^2$	99 **Es** $5f^{11}7s^2$	100 **Fm** $5f^{12}7s^2$	101 **Md** $5f^{13}7s^2$	102 **No** $5f^{14}7s^2$	103 **Lr** $5f^{14}6d^17s^2$

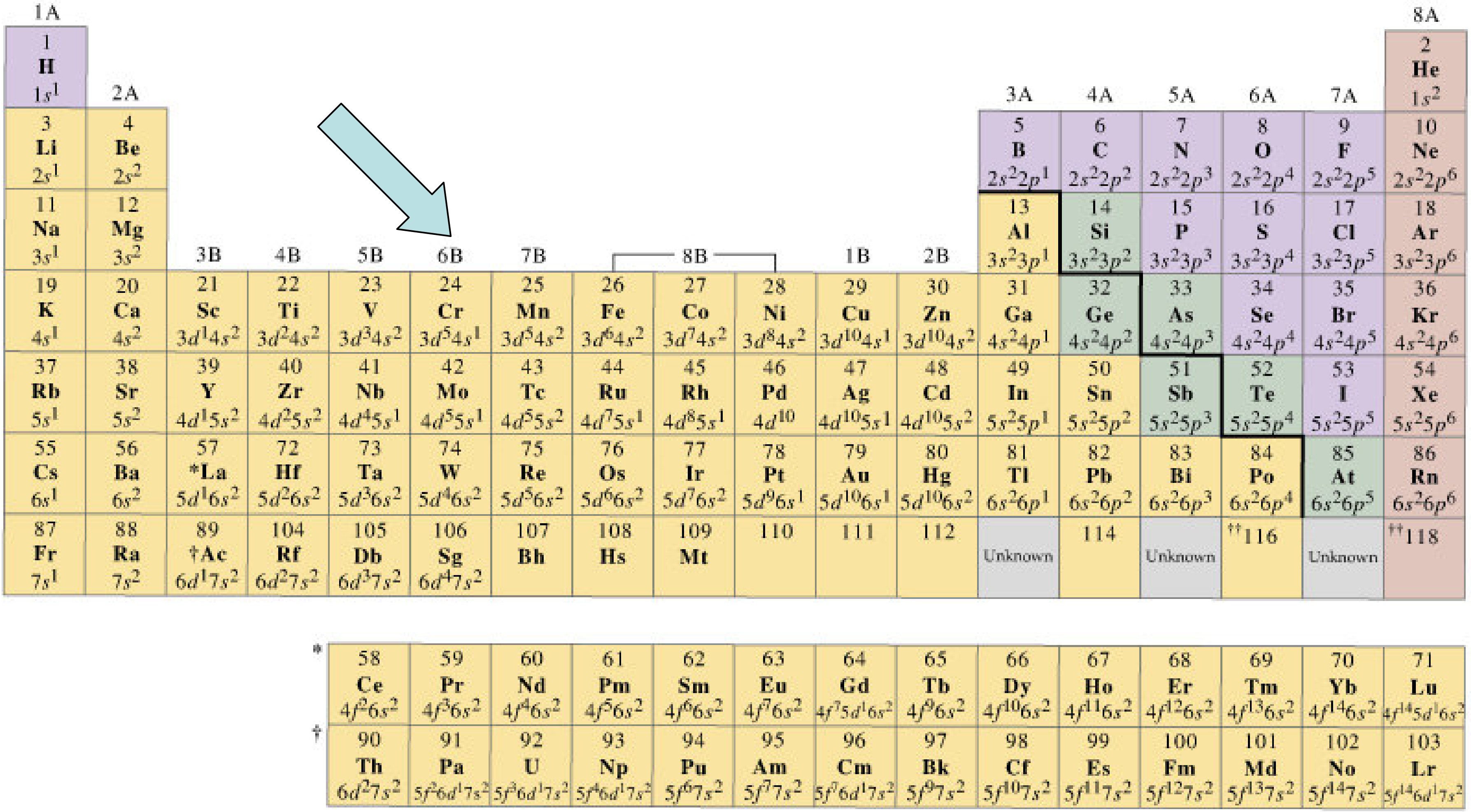
Cobalt
Ground State Electronic Configuration: [Ar].3d7.4s2



From the German word "kobald" meaning "goblin" or evil spirit. With an atomic number of 27, cobalt falls between iron and nickel on the periodic table. At temperatures below 417℃ cobalt exhibits a hexagonal close-packed structure. Between 417℃ and its melting point of 1493℃, cobalt has a face-centered cubic structure.

27
Co
58.933200

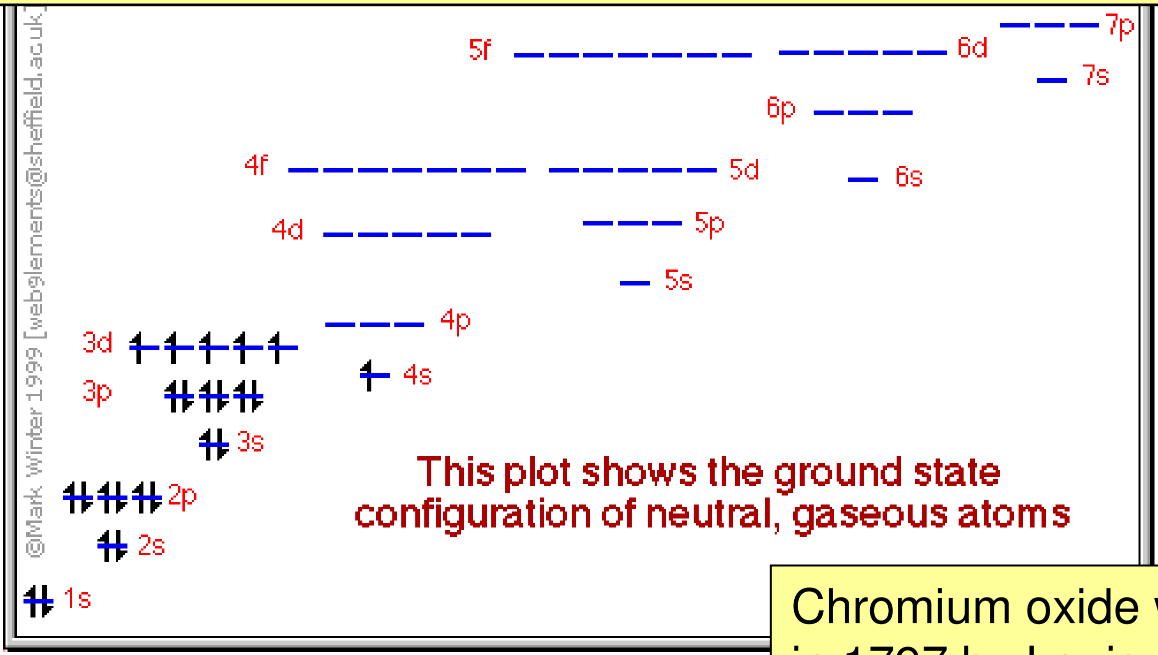
Periodic Chart of the Elements



1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
1 **H** $1s^1$																	2 **He** $1s^2$
3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^2 2p^1$	6 **C** $2s^2 2p^2$	7 **N** $2s^2 2p^3$	8 **O** $2s^2 2p^4$	9 **F** $2s^2 2p^5$	10 **Ne** $2s^2 2p^6$
11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^2 3p^1$	14 **Si** $3s^2 3p^2$	15 **P** $3s^2 3p^3$	16 **S** $3s^2 3p^4$	17 **Cl** $3s^2 3p^5$	18 **Ar** $3s^2 3p^6$
19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^1 4s^2$	22 **Ti** $3d^2 4s^2$	23 **V** $3d^3 4s^2$	24 **Cr** $3d^5 4s^1$	25 **Mn** $3d^5 4s^2$	26 **Fe** $3d^6 4s^2$	27 **Co** $3d^7 4s^2$	28 **Ni** $3d^8 4s^2$	29 **Cu** $3d^{10} 4s^1$	30 **Zn** $3d^{10} 4s^2$	31 **Ga** $4s^2 4p^1$	32 **Ge** $4s^2 4p^2$	33 **As** $4s^2 4p^3$	34 **Se** $4s^2 4p^4$	35 **Br** $4s^2 4p^5$	36 **Kr** $4s^2 4p^6$
37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^1 5s^2$	40 **Zr** $4d^2 5s^2$	41 **Nb** $4d^4 5s^1$	42 **Mo** $4d^5 5s^1$	43 **Tc** $4d^5 5s^2$	44 **Ru** $4d^7 5s^1$	45 **Rh** $4d^8 5s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10} 5s^1$	48 **Cd** $4d^{10} 5s^2$	49 **In** $5s^2 5p^1$	50 **Sn** $5s^2 5p^2$	51 **Sb** $5s^2 5p^3$	52 **Te** $5s^2 5p^4$	53 **I** $5s^2 5p^5$	54 **Xe** $5s^2 5p^6$
55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 ***La** $5d^1 6s^2$	72 **Hf** $5d^2 6s^2$	73 **Ta** $5d^3 6s^2$	74 **W** $5d^4 6s^2$	75 **Re** $5d^5 6s^2$	76 **Os** $5d^6 6s^2$	77 **Ir** $5d^7 6s^2$	78 **Pt** $5d^9 6s^1$	79 **Au** $5d^{10} 6s^1$	80 **Hg** $5d^{10} 6s^2$	81 **Tl** $6s^2 6p^1$	82 **Pb** $6s^2 6p^2$	83 **Bi** $6s^2 6p^3$	84 **Po** $6s^2 6p^4$	85 **At** $6s^2 6p^5$	86 **Rn** $6s^2 6p^6$
87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **†Ac** $6d^1 7s^2$	104 **Rf** $6d^2 7s^2$	105 **Db** $6d^3 7s^2$	106 **Sg** $6d^4 7s^2$	107 **Bh**	108 **Hs**	109 **Mt**	110	111	112	Unknown	114	Unknown	††116	Unknown	††118

*	58 **Ce** $4f^2 6s^2$	59 **Pr** $4f^3 6s^2$	60 **Nd** $4f^4 6s^2$	61 **Pm** $4f^5 6s^2$	62 **Sm** $4f^6 6s^2$	63 **Eu** $4f^7 6s^2$	64 **Gd** $4f^7 5d^1 6s^2$	65 **Tb** $4f^9 6s^2$	66 **Dy** $4f^{10} 6s^2$	67 **Ho** $4f^{11} 6s^2$	68 **Er** $4f^{12} 6s^2$	69 **Tm** $4f^{13} 6s^2$	70 **Yb** $4f^{14} 6s^2$	71 **Lu** $4f^{14} 5d^1 6s^2$
†	90 **Th** $6d^2 7s^2$	91 **Pa** $5f^2 6d^1 7s^2$	92 **U** $5f^3 6d^1 7s^2$	93 **Np** $5f^4 6d^1 7s^2$	94 **Pu** $5f^6 7s^2$	95 **Am** $5f^7 7s^2$	96 **Cm** $5f^7 6d^1 7s^2$	97 **Bk** $5f^9 7s^2$	98 **Cf** $5f^{10} 7s^2$	99 **Es** $5f^{11} 7s^2$	100 **Fm** $5f^{12} 7s^2$	101 **Md** $5f^{13} 7s^2$	102 **No** $5f^{14} 7s^2$	103 **Lr** $5f^{14} 6d^1 7s^2$

Chromium
Ground State Electronic Configuration: [Ar].$3d^5.4s^1$



Chromium oxide was discovered in 1797 by Louis-Nicholas Vauquelin. Heating this oxide in an oven in the presence of charcoal as a reducing agent gave the metal, chromium.

24
Cr
51.9961

Cobalt Based Alloy History

Many of the commercial cobalt-base alloys are derived from the cobalt-chromium-tungsten and cobalt-chromium-molybdenum ternaries first investigated by Elwood Haynes in the beginning of 20th century. He discovered the high strength and stainless nature of the binary cobalt-chromium alloy, and he later identified tungsten and molybdenum as powerful strengthening agents within the cobalt-chromium system. When he discovered these alloys, Haynes named them the Stellite alloys after the Latin stella (star), because of their star-like luster. Having discovered their high strength at elevated temperatures, Haynes also promoted the use of Stellite alloys as cutting tool materials.

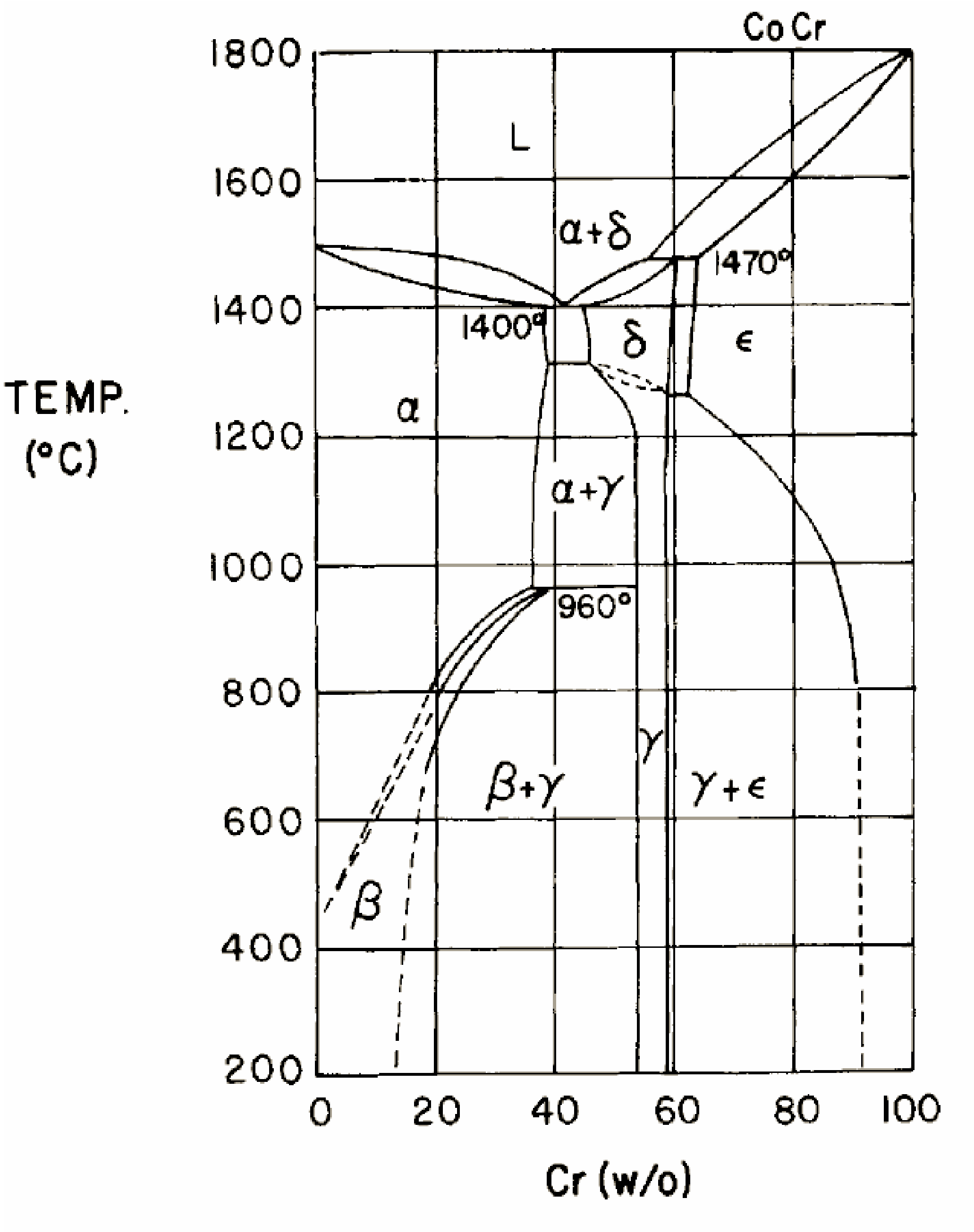
Cobalt Chromium Alloys

There are basically two types of cobalt chromium alloys. One is the cobalt CoCrMo alloy, which is usually used to cast a product and the other is the CoNiCrMo alloy, which is usually wrought by (hot) forging. The castable CoCrMo alloy has been used for many decades in dentistry and recently, in making artificial joints. The wrought CoNiCrMo alloy is now used for making the stems of prosthesis for heavily loaded joints such as the knee and hip. Cobalt-based alloys are highly resistant to corrosion and especially to attack by chloride. As in all highly alloyed metals in the body environment, galvanic corrosion can occur, but to a lesser extent than in the iron-based alloys.

Cobalt-based alloys are quite resistant to fatigue and to cracking caused by corrosion, and they are not brittle, since they have a minimum of 8% elongation. However, as is true of other alloys, cobalt based alloys may fail because of fatigue fracture (but less often than stainless steel stems). The superior fatigue and ultimate tensile strength of the wrought CoNiCrMo alloy make it suitable for the applications which require long service without fracture or stress fatigue. Such is the case for the stems of the hip joint prosthesis. The modulus of elasticity values are higher than other materials such as stainless steels.

Commercial Development of Cobalt Biomaterial

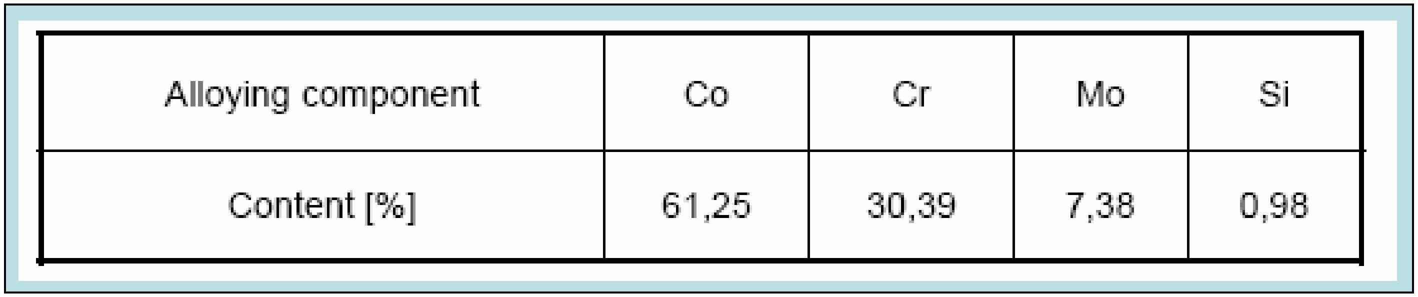
Drs. Reiner Erdle and Charles Prange founded Austenal Laboratories in 1926 to produce austenitic steel metal bases for full dentures. By 1932, Erdle and Prange were working with a new cobalt-chromium alloy that was showing great promise for strength and tarnish-resistance. The method of casting it, however, was radically different and required considerable training for laboratories to embrace this new technique. As its biocompatible properties were further understood, VITALLIUM was considered to be a miracle alloy, offering tremendous benefits not only for dental patients but for orthopedic patients as well. The demand for VITALLIUM grew rapidly, and with it the demand for training and further innovations.



The Cobalt alloys contain chromium for the same reason as stainless steel does, and ten times as much carbon as 316L, forming carbides that increase strength.

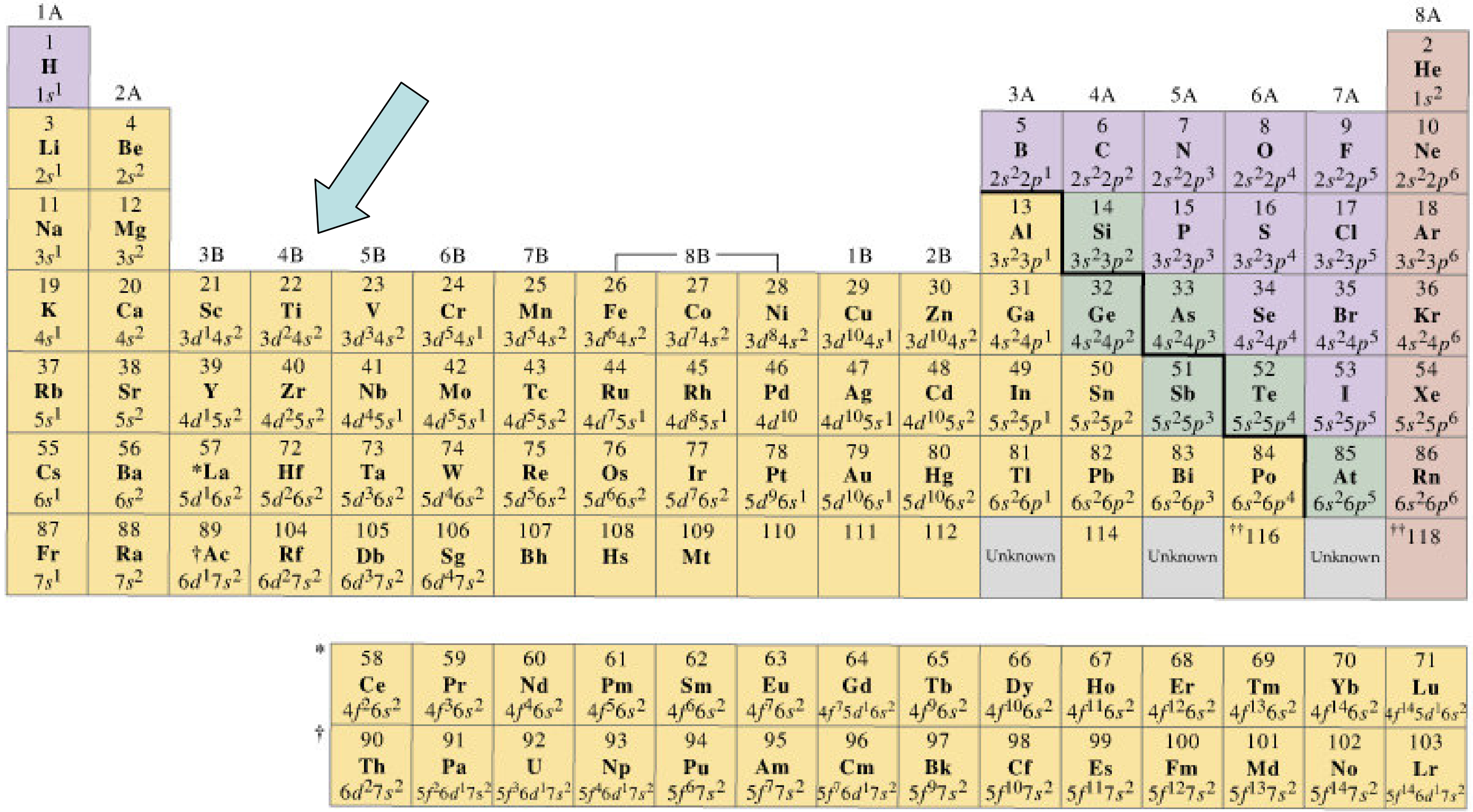
1937—Alvin Strock inserts the first Vitallium dental screw implant. Vitallium, the first successful biocompatible implant metal produced by Austenal.

1947 – Charles S. Venable and Walter G. Stuck publish, ***The Internal Fixation of Fractures,*** in which the authors introduced the trademarked alloy Vitallium into the field of bone surgery.



Alloying component	Co	Cr	Mo	Si
Content [%]	61,25	30,39	7,38	0,98

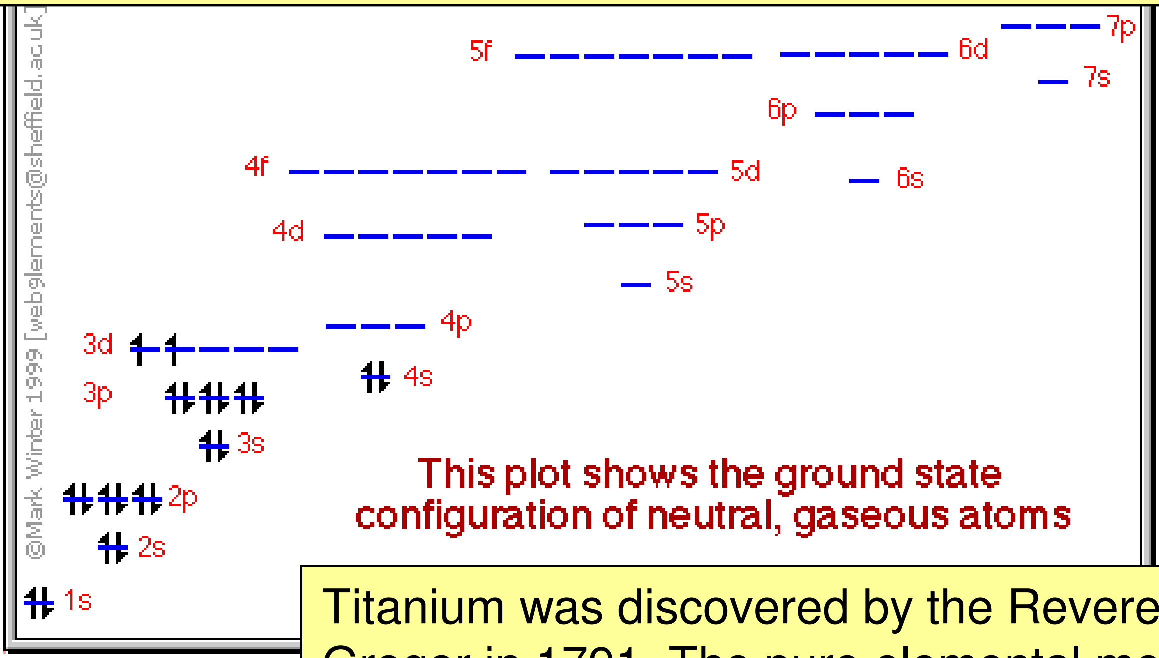
Periodic Chart of the Elements



1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
1 **H** $1s^1$																	2 **He** $1s^2$
3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	31 **Ga** $4s^24p^1$	32 **Ge** $4s^24p^2$	33 **As** $4s^24p^3$	34 **Se** $4s^24p^4$	35 **Br** $4s^24p^5$	36 **Kr** $4s^24p^6$
37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^45s^1$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	49 **In** $5s^25p^1$	50 **Sn** $5s^25p^2$	51 **Sb** $5s^25p^3$	52 **Te** $5s^25p^4$	53 **I** $5s^25p^5$	54 **Xe** $5s^25p^6$
55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 ***La** $5d^16s^2$	72 **Hf** $5d^26s^2$	73 **Ta** $5d^36s^2$	74 **W** $5d^46s^2$	75 **Re** $5d^56s^2$	76 **Os** $5d^66s^2$	77 **Ir** $5d^76s^2$	78 **Pt** $5d^96s^1$	79 **Au** $5d^{10}6s^1$	80 **Hg** $5d^{10}6s^2$	81 **Tl** $6s^26p^1$	82 **Pb** $6s^26p^2$	83 **Bi** $6s^26p^3$	84 **Po** $6s^26p^4$	85 **At** $6s^26p^5$	86 **Rn** $6s^26p^6$
87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **†Ac** $6d^17s^2$	104 **Rf** $6d^27s^2$	105 **Db** $6d^37s^2$	106 **Sg** $6d^47s^2$	107 **Bh**	108 **Hs**	109 **Mt**	110	111	112	Unknown	114	Unknown	††116	Unknown	††118

*	58 **Ce** $4f^26s^2$	59 **Pr** $4f^36s^2$	60 **Nd** $4f^46s^2$	61 **Pm** $4f^56s^2$	62 **Sm** $4f^66s^2$	63 **Eu** $4f^76s^2$	64 **Gd** $4f^75d^16s^2$	65 **Tb** $4f^96s^2$	66 **Dy** $4f^{10}6s^2$	67 **Ho** $4f^{11}6s^2$	68 **Er** $4f^{12}6s^2$	69 **Tm** $4f^{13}6s^2$	70 **Yb** $4f^{14}6s^2$	71 **Lu** $4f^{14}5d^16s^2$
†	90 **Th** $6d^27s^2$	91 **Pa** $5f^26d^17s^2$	92 **U** $5f^36d^17s^2$	93 **Np** $5f^46d^17s^2$	94 **Pu** $5f^67s^2$	95 **Am** $5f^77s^2$	96 **Cm** $5f^76d^17s^2$	97 **Bk** $5f^97s^2$	98 **Cf** $5f^{10}7s^2$	99 **Es** $5f^{11}7s^2$	100 **Fm** $5f^{12}7s^2$	101 **Md** $5f^{13}7s^2$	102 **No** $5f^{14}7s^2$	103 **Lr** $5f^{14}6d^17s^2$

Titanium
Ground State Electronic Configuration: [Ar].$3d^2$.$4s^2$



22

Ti

47.867

Titanium was discovered by the Reverend William Gregor in 1791. The pure elemental metal was not isolated until 1910 by Matthew A. Hunter, who heated TiCl4 together with sodium in a steel bomb at 700-800℃. Named after the "*Titans*", the sons of , Gaia, the earth goddess in Greek mythology: http://homepage.mac.com/cparada/GML/Cronos.html

Titanium and Titanium Based Alloys

Titanium is the most recent metallic biomaterial of the three main metallic biomaterials. While stainless steels and cobalt-based alloys are still the most widely used, titanium is increasingly being implemented in both medical and dental devices.

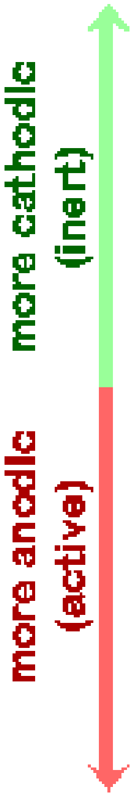
Titanium and its alloys are attractive metallic materials for biomedical applications because of improved biocompatibility, light weight, useful balance of mechanical properties and high corrosion resistance. They are largely used in for implant devices replacing failed hard tissue, for example, artificial hip joints, artificial knee joints, and bone plates. The metal and its alloys are also used for dental products such as crowns, bridges, and dentures, which are mainly produced by precision casting.

Titanium alloys were initially developed mainly for aerospace applications. Ti-6Al-4V alloys are the most used titanium alloys for biomedical applications, however no titanium alloys have been developed specifically for biomedical applications.

The Galvanic Series

- Ranks the reactivity of metals/alloys in seawater

Metals can be ranked in terms of their relative tendencies to release electrons in anodic processes.



Platinum
Gold
Graphite
Titanium
Silver
316 Stainless Steel (passive)
Nickel (passive)
Copper
Nickel (active)
Tin
Lead
316 Stainless Steel (active)
Iron/Steel
Aluminum Alloys
Cadmium
Zinc
Magnesium

Table 18.2, Callister (Partial list)

Production of Ti

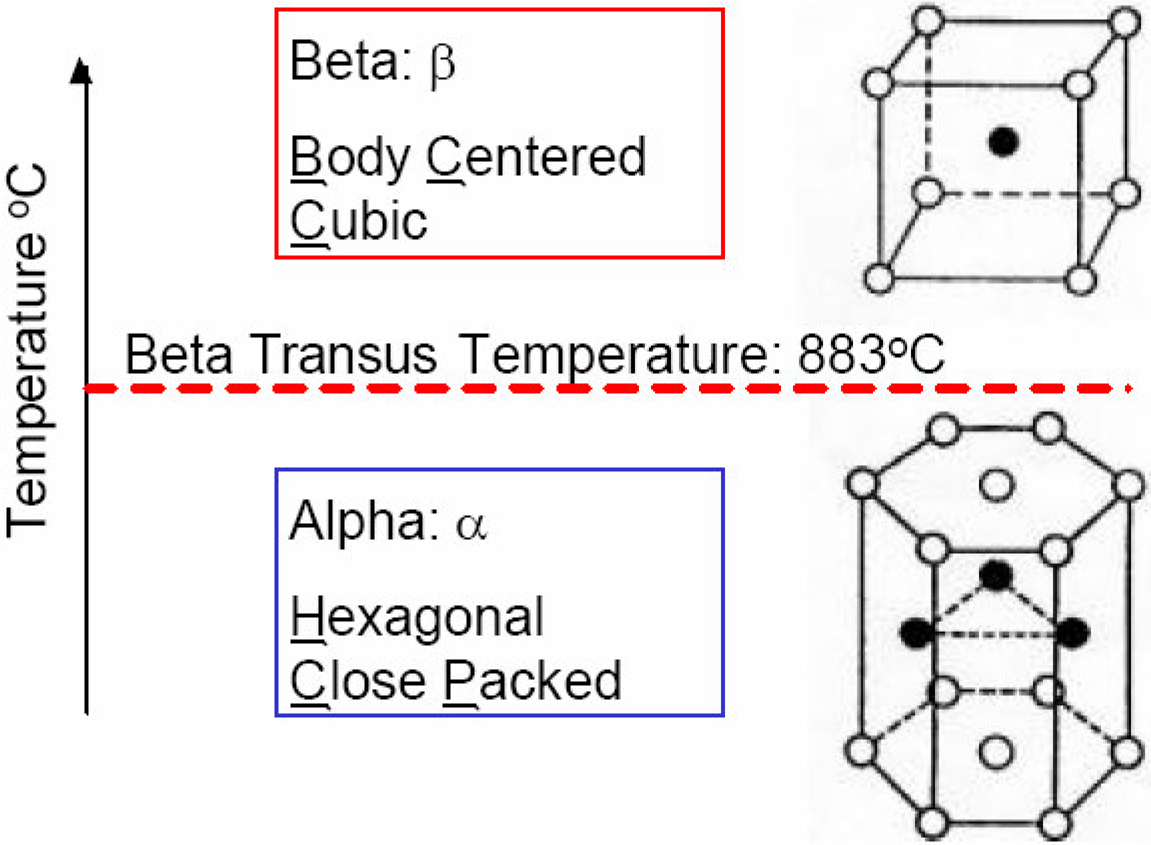
- Obtained from minerals:
  - rutile (TiO_2)
  - ilmenite ($FeO\text{-}TiO_2$) approx 97-98% TiO_2
- Chemically converted to pure $TiCl_4$
- Kroll Process:
  - $TiCl_4$ reacted with liquid Mg at ~773-873°C in a closed stainless-steel vessel (retort)
  - $4TiCl_{4\ (gas)} + 2Mg_{\ (liquid)} \rightarrow \underset{\substack{\downarrow \\ \text{Ti sponge}}}{Ti}_{\ (solid)} + 2MgCl_{2\ (liquid)}$

The Kroll Process is an industrial process used produce metallic titanium invented in 1940 by William J. Kroll, at the Albany Research center in Oregon.

“Pure” Titanium

Titanium is allotropic. In pure titanium at lower temperatures, the crystals have a structure or a "unit cell type" that is known as "close-packed hexagonal" or cph. The cph crystal shape is the originally observed or "alpha" phase. When the temperature of titanium is raised above 883° centigrade (1620° F) yet below 1727℃ (3140℉), the titanium crystal changes by allotropic transformation into to a "body centered cubic" or bcc crystal structure or unit cell type. The bcc unit cell structure is referred to as its "beta" phase. This change to a bcc crystal structure remains only while the temperature is in this range, and reverts to the cph type when cooled down below this range. The allotropic transformation temperature also known as the "beta transus" is affected by the amount and type of impurities in the titanium.

Allotropic forms of pure titanium



Temperature °C

Beta: β

Body Centered Cubic

Beta Transus Temperature: 883°C

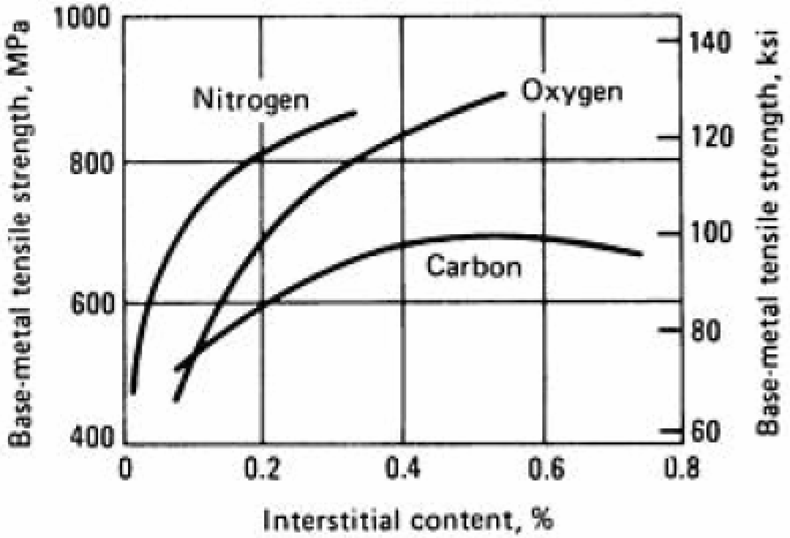
Alpha: α

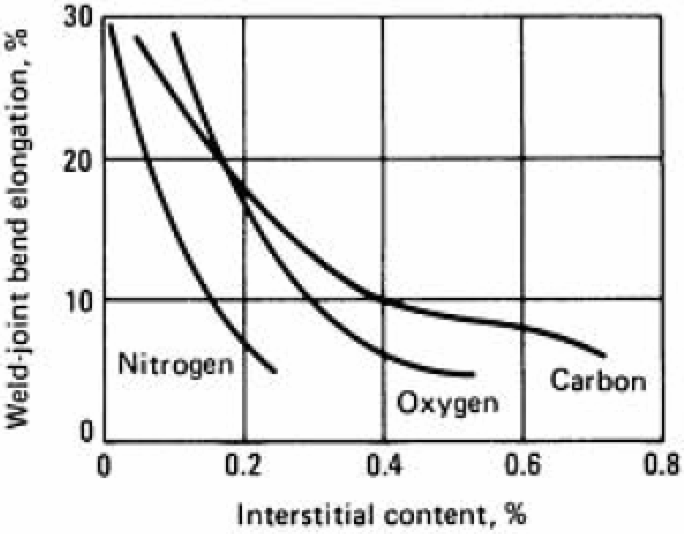
Hexagonal Close Packed

Commercially Pure Titanium

Commercially pure (CP) titanium alloys consist of alpha alloys with extremely low amounts of what are called "interstitial" elements used as alloy elements. The interstitial atoms are generally non-metallic, in the case of alpha titanium alloys they are nitrogen, oxygen, and carbon. The primary difference between the various grades of commercially pure titanium is the content or amount of this interstitial element in the alloy. Alloys that have a higher purity, (less solute or interstitial element alloyed in the titanium), have lower strength, lower hardness and a lower alpha-beta transformation temperature. Commercially pure titanium alpha alloys are referred to by their American Society for Testing and Materials (ASTM) "grade" designation number. There are five grades of what is known as commercially pure or unalloyed titanium, ASTM Grades 1 through 4, and 7. Each grade has a different amount of impurity content, with Grade 1 being the most pure. Tensile strengths vary from 172 MPa for Grade 1 to 483 MPa for Grade 4.

Interstitials effects



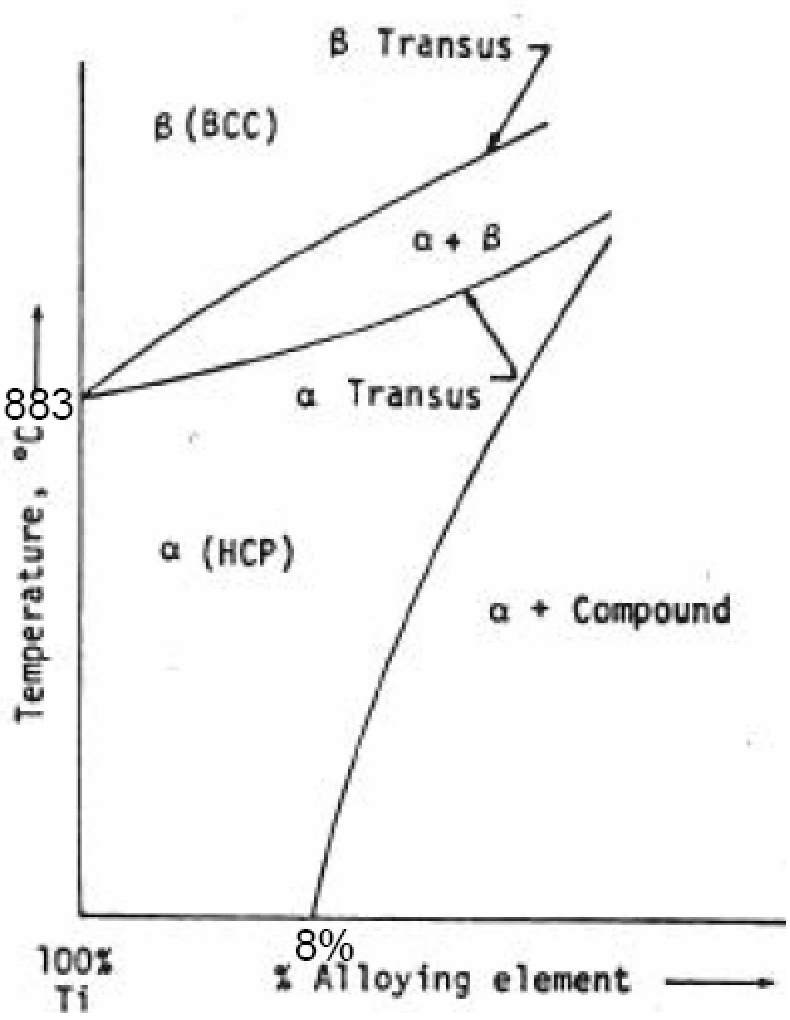


Titanium Alloy Types

1. Alpha alloys- They have low to medium strength, good notch toughness, reasonably good ductility and have excellent properties at cryogenic temperatures. The more highly alpha or near alpha alloys offer high temperature creep strength and oxidation resistance.

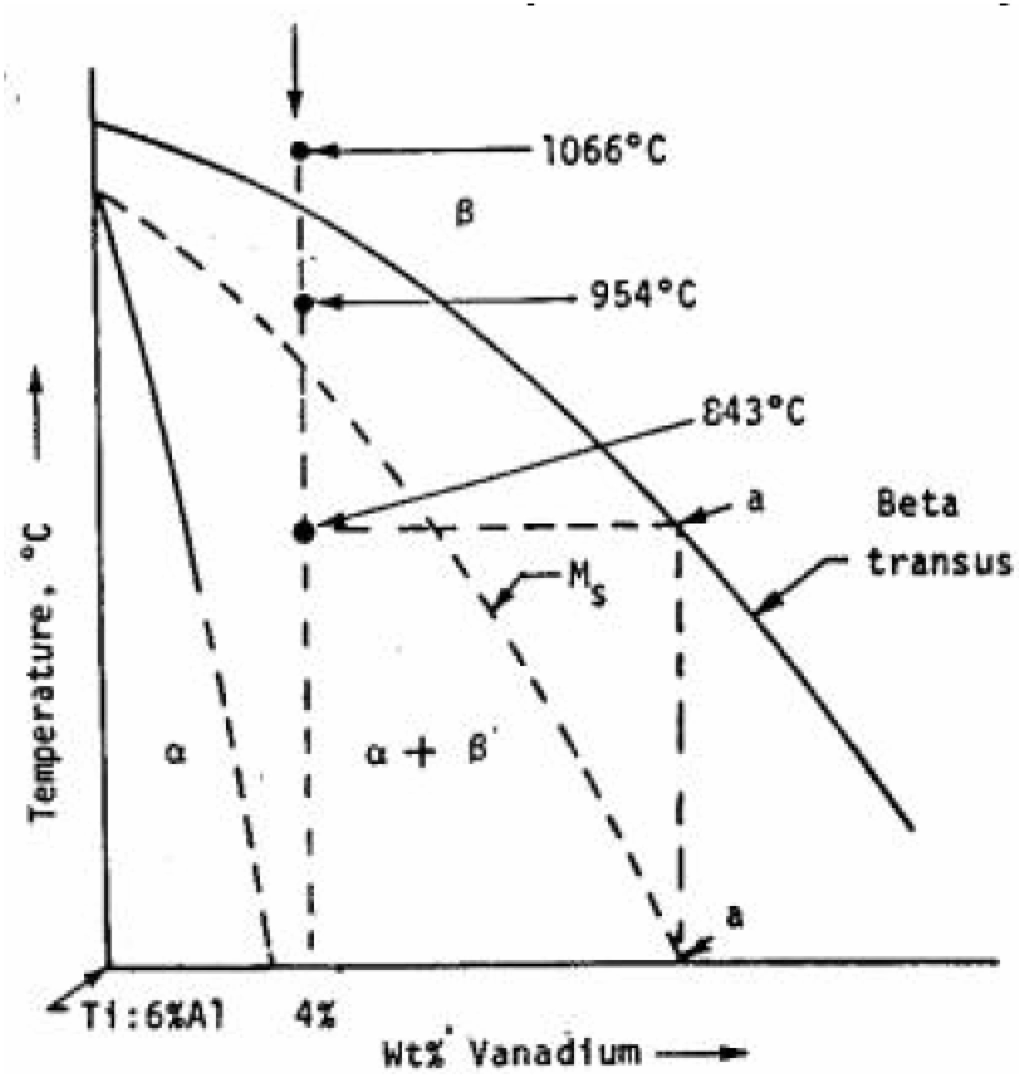
2. Alpha+Beta alloys- Their strength levels are medium to high. Hot forming qualities are good but cold forming often presents difficulties. Creep strength is not usually as good as in most alpha alloys.

3. Beta alloys- They offer high strength up to intermediate temperature levels. In the solution treated condition, cold formability is generally excellent.



Alpha-Titanium Alloy

Aluminum stabilizes the alpha phase (hcp). The alpha field is extended and the beta transus is increased in temperature from 883℃ with increasing Al content. Higher levels of Al result in the formation of an alpha-2 phase, Ti_3Al, which leads to embrittlement.



For Ti-6%Al alloy with additions of Vanadium

alpha + beta Ti Alloys

60% of all Ti usage is in the form of the alloy: Ti-6%Al-4%V. Al stabilizes the alpha-phase and V stabilizes the beta-phase

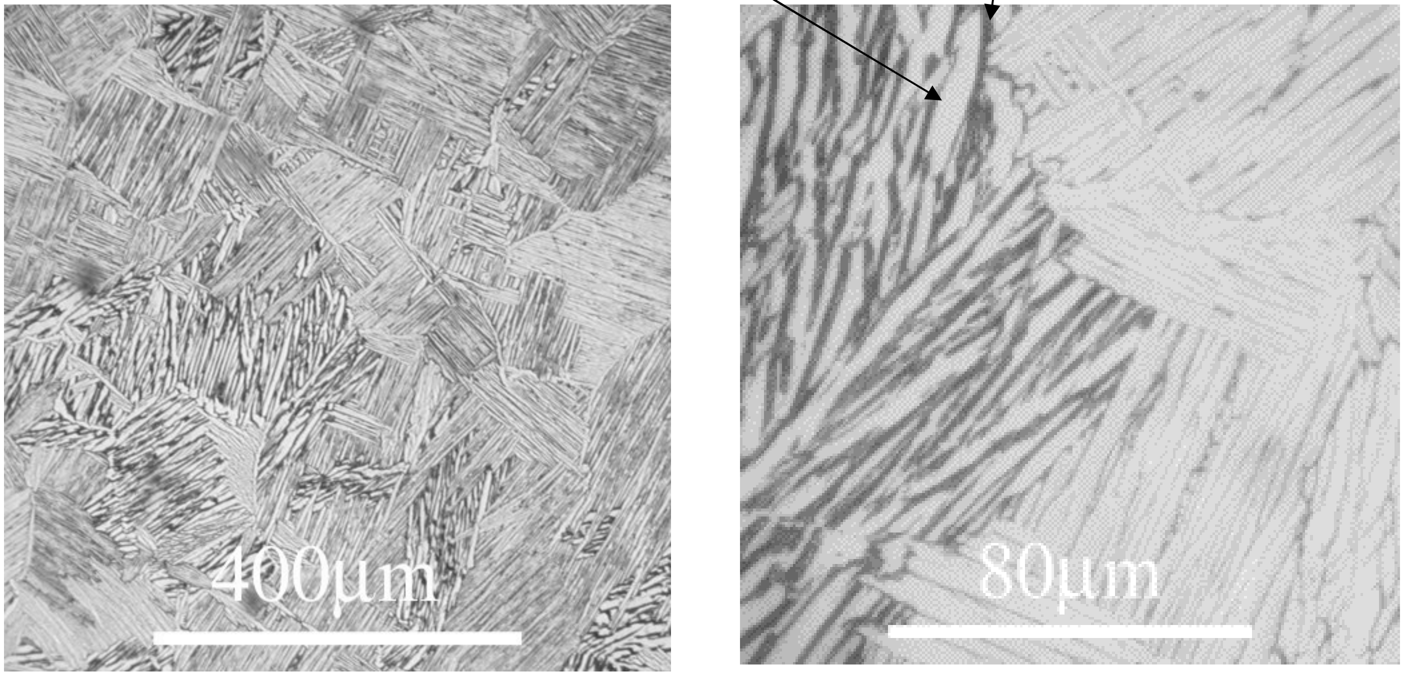
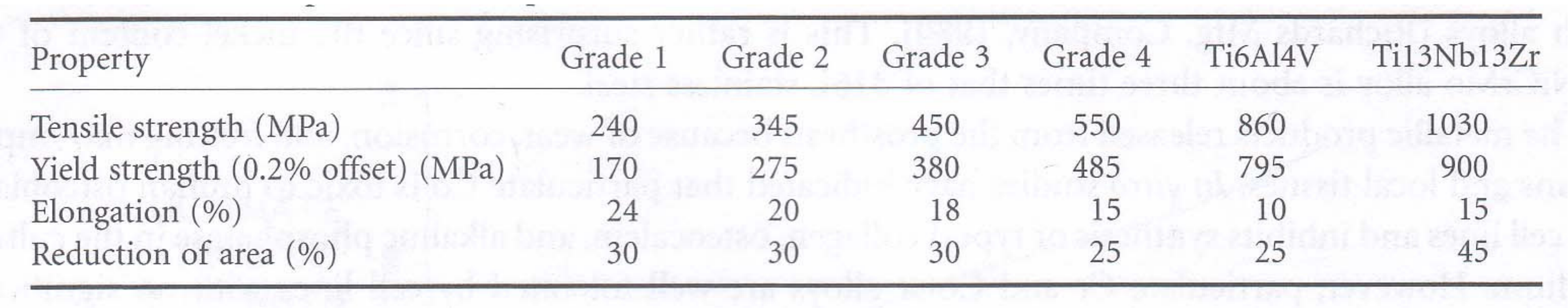


Plate-like alpha (light hcp)

Intergranular beta (dark bcc)

The detailed microstructure of Ti-6Al-4V will depend on the thermomechanical treatment

Titanium and Titanium Alloy Properties



Property	Grade 1	Grade 2	Grade 3	Grade 4	Ti6Al4V	Ti13Nb13Zr
Tensile strength (MPa)	240	345	450	550	860	1030
Yield strength (0.2% offset) (MPa)	170	275	380	485	795	900
Elongation (%)	24	20	18	15	10	15
Reduction of area (%)	30	30	30	25	25	45

Metal Toxicity

The subject of metal toxicity is in some ways difficult to assess because of the lack of agreement that sometimes exists in the technical literature on this subject.

It has been asserted that some metal toxic responses require that a threshold level be reached. However, some studies suggest that the continued exposure to low level metal corrosion and dissolution products can cause a toxic response.

Another problem is latency. In humans latency periods can be up to 15-20 years. The vast majority of implants have been in patients for only 15 or fewer years because of the advanced years of the receiving patient and the relative infancy of the technology. Thus, the appearance of metal toxicities may not manifest themselves.

Response to metal and their corrosion products can be relatively minor. Some people develop dermatitis (also called eczema) from even brief contact with nickel-containing items, while others break out only after many years of skin contact with nickel.

Inhibition of T/B Cell Proliferation by Ti, Co & Cr

Although metal cytotoxicity is not observed judging by cell viability and cell injury after human peripheral blood mononuclear cells were extensively exposed to metals, Phytohemagglutinin (PHA)-induced T-cell proliferation and lipopolysaccharide-induced B-cell proliferation were significantly inhibited by titanium, chromium and cobalt. Titanium did not alter IFN-gamma production, whereas chromium and cobalt significantly reduced IFN-gamma release by PHA-stimulated PBMC. The addition of IL-2 and IL-6 significantly restored the metal-induced inhibition of T-cell and B-cell proliferation, respectively. This study sheds light on how the metals impair immune response and cytokine release, suggesting that patients with an extensive exposure to the metals may develop immune dysfunctions. The compromised immune response induced by the metals might significantly contribute to an increased risk of infection in patients with joint prostheses.

(J Biomed Mater Res. 1996 Dec;32(4):655-61)

Foreign Body Carcinogenesis

Rather than the chemical nature of an implant, investigators have found that the physical form of the implant can dictate its carcinogenicity. The effect is called foreign body carcinogenesis. Solid materials without chemical carcinogenic activity can induce a variety of neoplasms in several small rodent species, and the larger the implant, the increase likelihood of carcinogenesis. Surprisingly, the carcinogenic potential can be inversely proportional to the inflammatory response; that is to say, well tolerated biomaterials in the long run were more efficient carcinogens.

The theory of foreign body carcinogenesis is that as cell damage occurs, some cells are favored in the presence of the solid body and protected from physiological processes until they are ready to enter the rapid growth phase characteristic of malignancy. One explanation of this is that as a cell abuts an implant, its area for microvascular supply, diffusional supply and cell contact inhibition decrease, therefore altering its steady state. From this altered steady state malignant transformation can occur.

Hard Tissue Mechanical Property Mismatch

The strongest metal is not necessarily the best metal to use. When using metals in bone replacement therapies “stress-shielding” can lead to undesired results. This occurs if the implant overly shields the bone from stress that it would normally experience. Under these conditions, the bone can be resorbed or broken down by the body, resulting in bone loss for the patient. On the other hand, if the bone is required to take on too much stress, abnormal growth can occur – called “adaptive remodeling.”

http://www.owlnet.rice.edu/~bioe372/Project-2006.html

Implant loosening after years of wear. Picture courtesy of Schulthess Klinik, Switzerland.

Improved Design of Cementless Hip Stems Using Two-Dimensional Functionally Graded Materials

H. S. Hedia, M. A. N. Shabara, T. T. El-Midany, N. Fouda

Department of Production Engineering and M/C Design, Faculty of Engineering, Mansoura University, Mansoura, Egypt

Journal of Biomedical Materials Research Part B: Applied Biomaterials
DOI 10.1002/jbmb

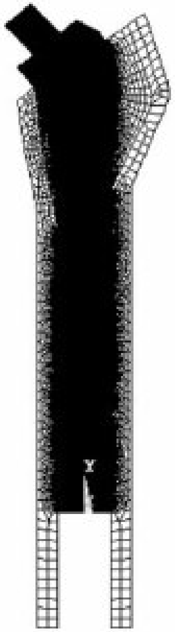


Figure 4. The finite element mesh for the endoprosthesis.

For modulus of elasticity,

$$E = \frac{E_{xy}(1 - p_y)}{1 + p_y(5 + 8v)(37 - 8v)/\{8(1 + v)(23 + 8v)\}} \quad (10)$$

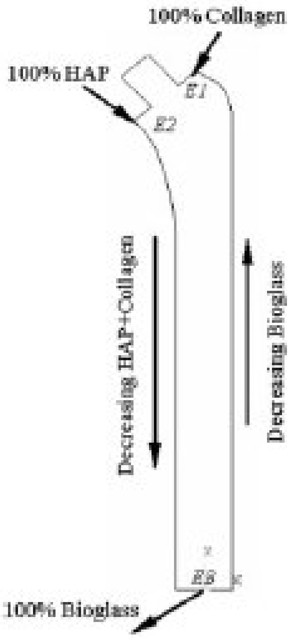
where,

$$E_{xy} = E_x\left[\frac{E_x + (E_3 - E_x)V_3^{2/3}}{E_x + (E_3 - E_x)(V_3^{2/3} - 1 + V_x)}\right] \quad (11)$$

$$E_x = \frac{E_{ax}(1 - p_x)}{1 + p_x(5 + 8v_x)(37 - 8v_x)/\{8(1 + v_x)(23 + 8v_x)\}} \quad (12)$$

$$E_{ax} = \left[\frac{E_1 + (E_2 - E_1)V_2^{2/3}}{E_1 + (E_2 - E_1)(V_2^{2/3} - V_2)}\right] \quad (13)$$

$$v_x = v_1V_1 + v_2V_2 \quad (14)$$



Two-dimensional FGM is made of continuous gradation of three distinct material phases. It is fabricated in such a way that the volume fractions of the constituents are varied continuously in a predetermined composition profile. In design-

This design (model I) is expected to reduce the stress shielding at the proximal medial part of the femur by about 91% compared with titanium stem. However, the maximum interface shear stress is reduced by about 50% for both the medial and lateral sides of the femur compared with that of the titanium stem.

Summary

1. There are three classes of metal alloys used in implant applications; stainless steel, cobalt chrome alloys and titanium/titanium alloys.

2. Plastic deformation occurs in metals by the movement of dislocations. Strength of metals can be increased by inhibiting dislocation motion.

3. Metal corrosion is an electrochemical phenomenon.

4. There are three types of corrosion cells: composition, stress and concentration.

5. Austenitic stainless steel (316 and 316L) is historically the most widely used metal used for implant applications.

6. “Vitallium” was the first cobalt-based alloy to be used for implants: Co:61.25, Cr:30.39, Mo:7.38, Si:0.98.

7. Ti-6Al-4V alloy is a alpha+beta-alloy and the most widely used titanium composition.