Chapter 9. Alloys

Alloy:
• homogeneous combination of 2 or more elements
• at least one of which is a metal
• has metallic properties

Based on Fe	Based on other metals (Al, Cu, Mg, Ti, Ni)
ferrous	**nonferrous**

• Need to improve some properties of the base metal

Density, reactivity, electrical and thermal conductivity is often the same as a constituent metal

Mechanical properties (strength, Young's modulus, etc.) can be very different

• Comparative cost of the element components

Steel:	\$0.27 /lb	Cu: \$0.76 / lb	Al: \$0.67 /lb	Zn: 0.45 /lb	(2001)
	\$0.36 /lb	\$3.62 / lb	\$1.14 /lb	1.34 /lb	(2007)

9.1 Iron and Steel

First step: Fe extraction in **blast** furnaces (reduction reaction at ~400^oC):

• main iron ore: Fe_2O_3

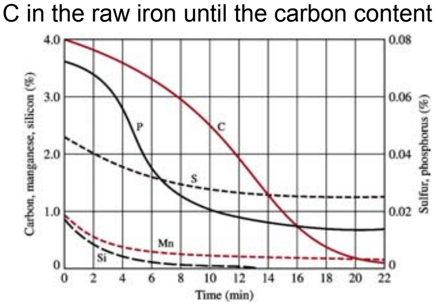
• resulting raw iron is molten: Fe (~4% C) $\Rightarrow$ **steel-making** furnace

Steel: alloy of Fe and C (up to 1.2%)

$\Rightarrow$ oxidize impurity (S, P, etc) and C in the raw iron until the carbon content is below the required level

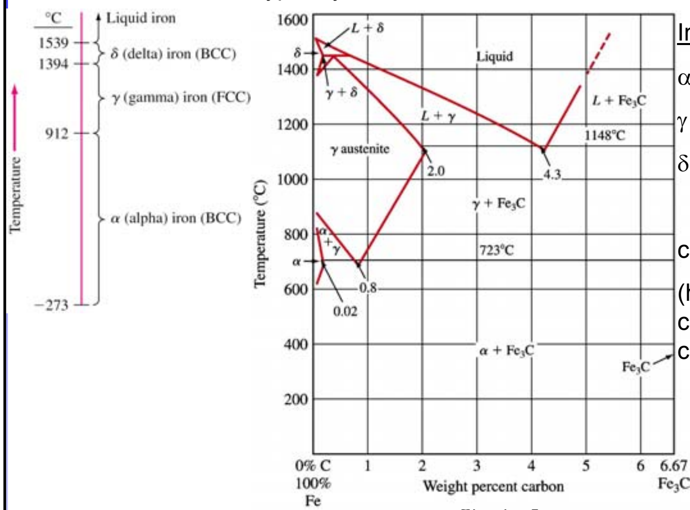
$Fe_2O_3 + 3\ C = 2\ Fe + 3\ CO$

$FeO + C = Fe + CO$



9.2 The Fe-C System

Plain-carbon steel: typically 0.03-1.2% C, 0.25-1% Mn, + other minor impurities



<u>Interstitial s. s. solutions</u>

α ferrite – Fe (0.02%C)

γ – austenite Fe (2.08%C)

δ - ferrite (0.09% C)

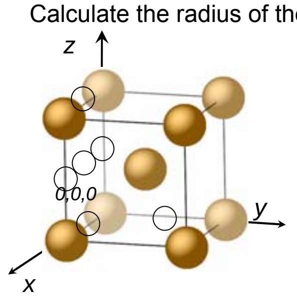
cementite - Fe_3C

(hard and brittle compound, different crystal structure)

Interstitial voids in the *bcc* α Fe lattice

Consider bcc α Fe lattice, the atomic radius of the Fe is 0.124nm, and the largest interstitials are at the ($^1/_2$, 0, 0), (0, ½, 0), (0, 0, ½), (½, ½, 0), *etc.* positions

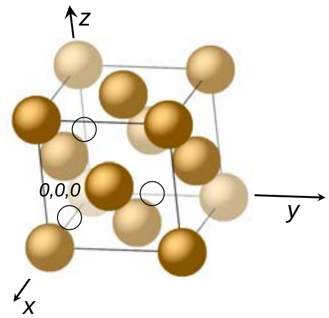
Calculate the radius of the largest interstitial voids.



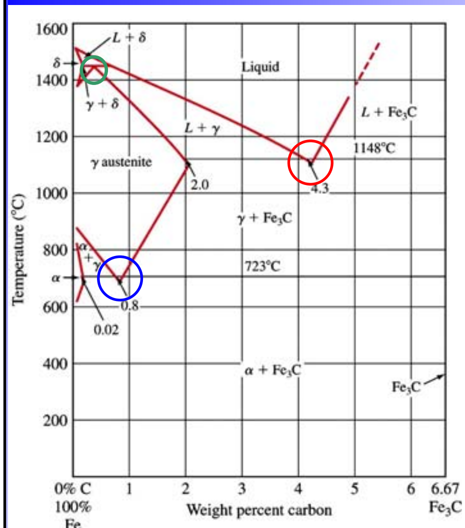
Interstitial voids in the *fcc* γ Fe lattice

Consider fcc γ Fe lattice, the atomic radius of the iron in 0.124nm, and the largest interstitials occur at the ($^1/_2$, 0, 0), (0, ½, 0), (0, 0, ½), *etc.* type positions

Calculate the radius of the largest interstitial voids.



Invariant reactions in the Fe-Fe_3C diagram

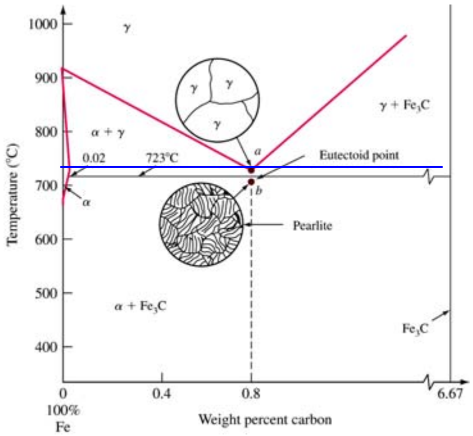


Eutectic composition – a specific alloy composition that freezes at a **lower** than all other composition

Eutectic temperature – the **lowest** temperature at which the L phase can exist when cool down slowly

Eutectoid plain carbon steel

Take 0.8% C steel, heat it slightly above 750^{o}C, start to **cool very slowly** $\rightarrow$ austenite (γ phase) formation if we wait long enough



Q: A 0.8%C plain-carbon steel is slowly cooled from 750^{o}C to a temperature lightly < 723^{o}C. Assuming that the austenite is completely transformed to α and Fe_3C. Calculate the weight percent (W, %) eutectoid α and Fe_3C formed.

Hypoeutectoid and hypereutectoid compositions

0.4% eutectoid 0.8% 1.2%

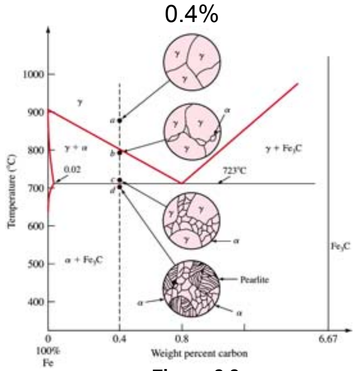


Figure 9.9

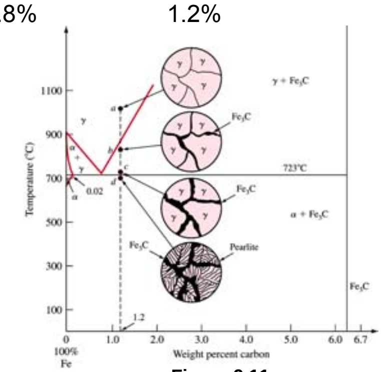
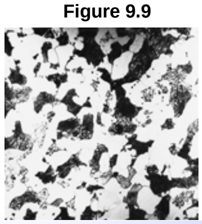
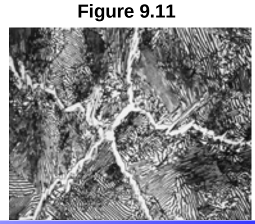


Figure 9.11





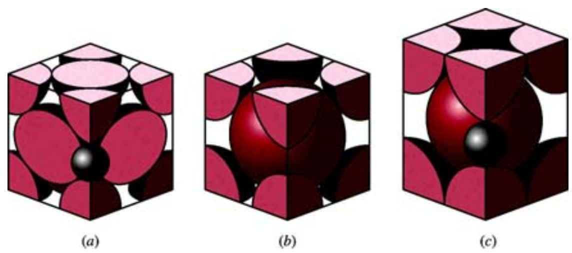
9.3 Heat treatment of plain-carbon steel

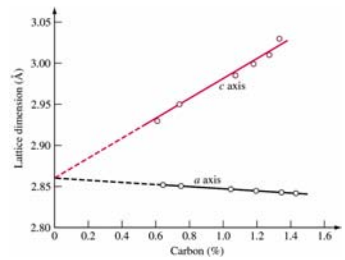
Different **mechanical properties** of steel can be obtained by variation of **heating** and **cooling** rate

Take 0.8% C steel, heat it slightly above 750°C, **rapidly cool (quench)** → *martensite* phase formation

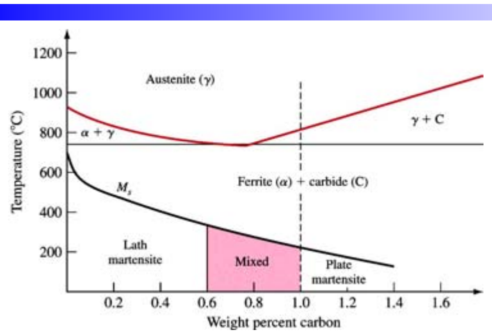
γ (austenite) phase – s.s.s. C in γ *fcc* Fe

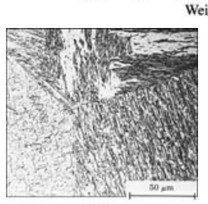
M (martensite) phase – supersaturated s.s.s. C in *bcc* Fe or tetragonally distorted *bcc* Fe: metastable phase



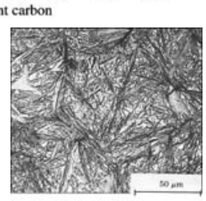


Martensite microstructure and mechanical properties

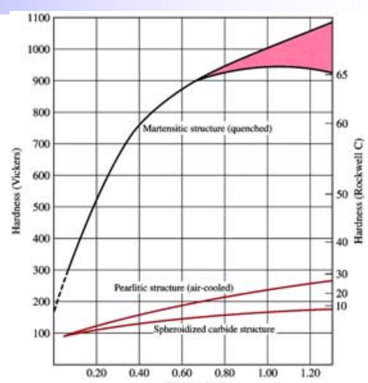




< 0.6% C lath domains

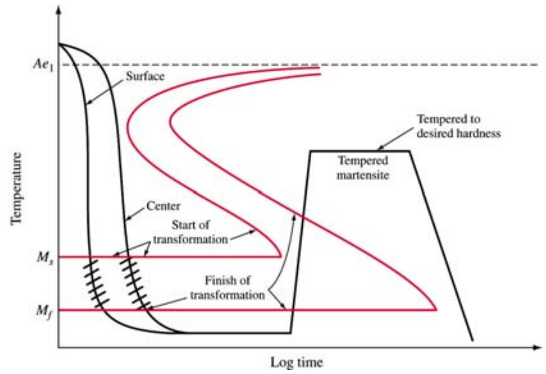


> 1% C plate domains



Steel tempering

Tempering: heating a martensitic steel at T < the eutectoid transformation temperature (723^{o}C) to make it softer and more ductile



9.4 Classification of plain-carbon steels

Designated by a four-digit AISI-SAE* code: 10XX

“10” : plain – carbon steel

“XX” : the nominal carbon content of the steel in hundredths of a percent (0.3% C - 1030)

Alloy AISI-SAE number	Chemical composition (wt %)	Condition	Tensile strength ksi	Tensile strength MPa	Yield strength ksi	Yield strength MPa	Elongation (%)
1010	0.10 C, 0.40 Mn	Hot-rolled	40–60	276–414	26–45	179–310	28–47
		Cold-rolled	42–58	290–400	23–38	159–262	30–45
1020	0.20 C, 0.45 Mn	As rolled	65	448	48	331	36
		Annealed	57	393	43	297	36
1040	0.40 C, 0.45 Mn	As rolled	90	621	60	414	25
		Annealed	75	517	51	352	30
		Tempered*	116	800	86	593	20
1060	0.60 C, 0.65 Mn	As rolled	118	814	70	483	17
		Annealed	91	628	54	483	22
		Tempered*	160	110	113	780	13
1080	0.80 C, 0.80 Mn	As rolled	140	967	85	586	12
		Annealed	89	614	54	373	25
		Tempered*	189	1304	142	980	12

- Mn enhances strength (0.3-0.95%)
- Low C content plain-carbon steels have low strength, but high ductility
- Low corrosion and oxidation resistance ⇒ alloying for another metals

* **American Iron and Steel Industry – Society for Automotive Engineers**

Classification of Alloy Steels

May contain up to 50% of alloying elements

Designated by 4 digit number "ABXX"

"AB" : principal alloying elements (or group of elements)

"XX" : the nominal carbon content of the steel in hundredths of a percent

5040 – Chromium (0.4%), C (0.4%); other examples in **Table 9.4**

Depending on the tendency to form the compound (oxide, sulfide, etc.) or carbide, alloy elements distribute themselves differently in steel (Table 9.5)

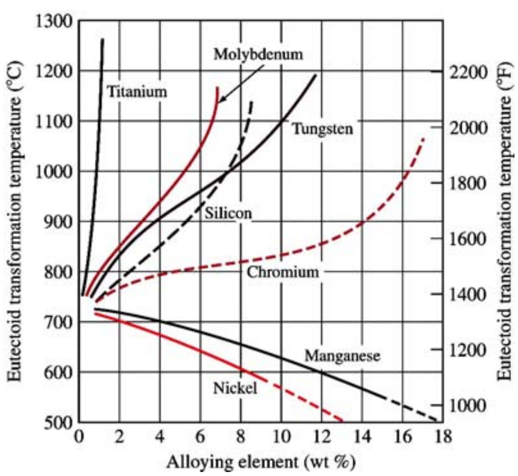
Cu – dissolves in ferrite (Fe)

Ni - dissolves in Fe, forms Ni_3Al (if Al is another alloying element)

Cr, Mo, W – dissolve in small amounts, compete with Fe to form M_xC

Si – dissolves in Fe, forms nonmetallic silicate (SiO_2)(M_xO_y) inclusions

Effect of Alloying Elements on the Eutectoid Temperature



The effect of the percentage of alloying elements on the eutectoid temperature

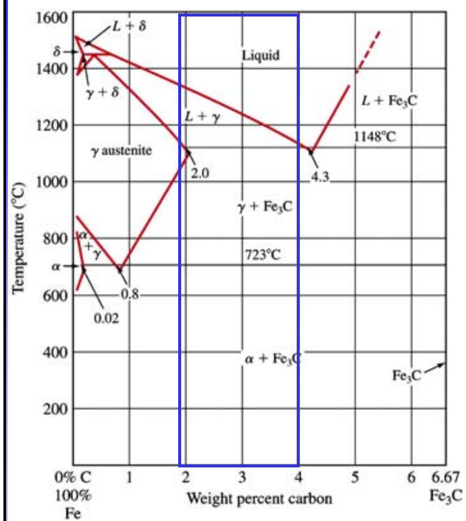
Ti, Mo and W – increase the T

(ferrite-stabilizing elements)

Mn and Ni – lower the T

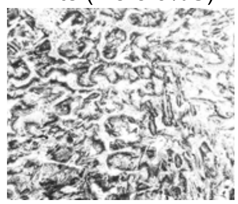
(austenite-stabilizing elements)

9.8 Cast Iron

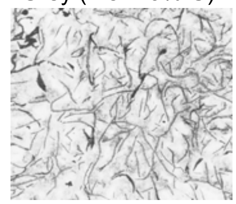


1.8-4.0% C, 0.5-3.0% Si, Mn, S, P

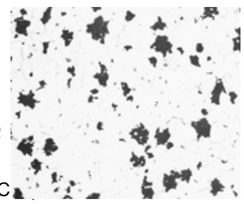
White (1.8-3.6%C)



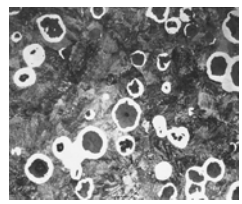
Grey (2.5-4.0% C)



Malleable (2.0-2.6%C)



Ductile (3.0-4.0% C)



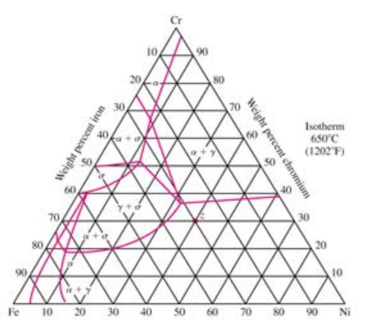
C

9.7 Stainless Steels

Stainless steel: Fe, **Cr**, Ni
High corrosion resistance - due to high Cr content (min 12% Cr)

Classical mechanism:

- low permeability to oxygen (low diffusion coefficients for metal ions and O)
- high plasticity to prevent fracture
- high melting T and low vapour p



S. steel is exposed to oxidizing agents to form a protective oxide layer

Ferritic s.s.: Fe-Cr alloys

Martensitic s.s.: Fe – Cr (12-17% Cr) – C (0.5-1%)

Austenitic s.s.: Fe – Cr - Ni

Fe retains *fcc* structure due to Ni (*fcc*) at RT

16

Sword construction

Unique hard, highly razor sharp cutting edge

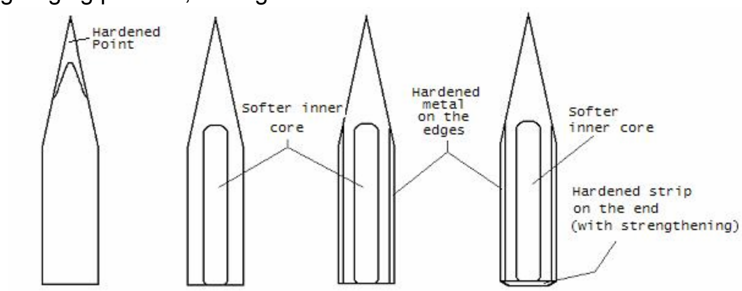
Inner core is resilient and is able to absorb shocks

Different steel types:

(1) softer inner core – lower C content

(2) harder outer shell

Long forging process, folding inner core into outer harder shell



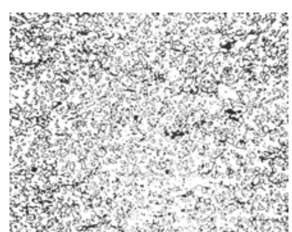
Is stainless steel good enough for swords?

If use the same:

- stays sharp for a long time, but will break as soon as you stress it
- very soft and tough, but dulls very easily
- most pronounced effect for the longer blades

Cr (smaller amounts): improves hardening and helps to refine the grain size

Cr (larger amounts): the grain boundaries are weakened $\Rightarrow$ affects the overall performance



440C (martensitic s.s)

- either toughness or edge-holding capabilities are compromised
- thicker to improve strength $\Rightarrow$ weight and balance problems
- durability

9.5 Aluminum Alloys

Parent metal Al:

+ low density (2.7 g/cm^3) $\Rightarrow$ transportation
+ excellent corrosion resistance (surface passivation by Al_2O_3 layer)
+ nontoxic $\Rightarrow$ food containers and packaging
+ high electrical conduction (Ag > Cu > Au > Al > …)
+ most abundant metallic element
+ relatively low price
- low strength $\Rightarrow$ but it can be alloyed!!!

Aluminum ores: $(Al_2O_3)_x(H_2O)_y$; $(Al_2O_3)_m(SiO_2)_n$; $(Al_2O_3)_x(Fe_2O_3)_y(H_2O)_z$

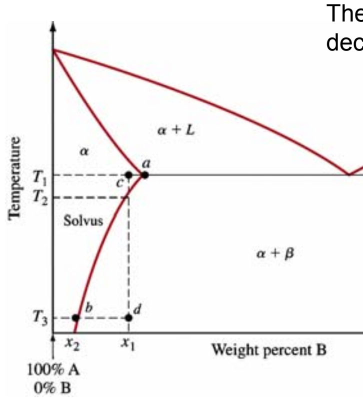
$$Al_2O_3 + H_2O + NaOH \Rightarrow Na\,[Al(OH)_4] \Rightarrow Al(OH)_3 \downarrow \Rightarrow Al_2O_3$$

Electrolysis (C cathode and anode, extremely high energy consumption)

Precipitation Strengthening (Hardening)

Using temperature cycling create a material (alloy) with a dense and fine dispersion of precipitated particles in a matrix of *deformable* metal (e.g. Al)

There must be a terminal solid solution with decreased solid state solubility as the T↓



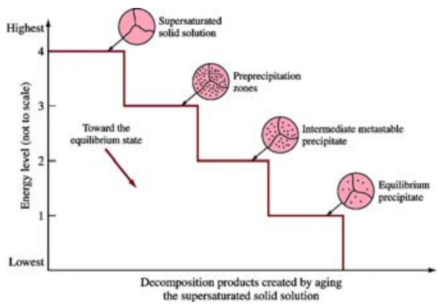
1. **Solution heat treatment** (to T between solvus and solidus, T_1)
2. **Quenching** (typically to RT, T_3): formation of supersaturated solid state solution
3. **Aging:** formation of finely dispersed precipitates

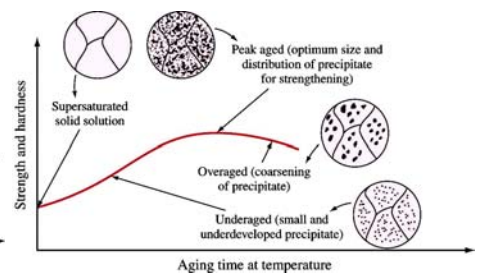
- natural aging (at RT)
- artificial aging (at ~0.15-0.25 (T_1-T_3))

Aging Process

Supersaturated solid solution: not a stable energy configuration

Formation of equilibrium or metastable phases lowers the energy of the system

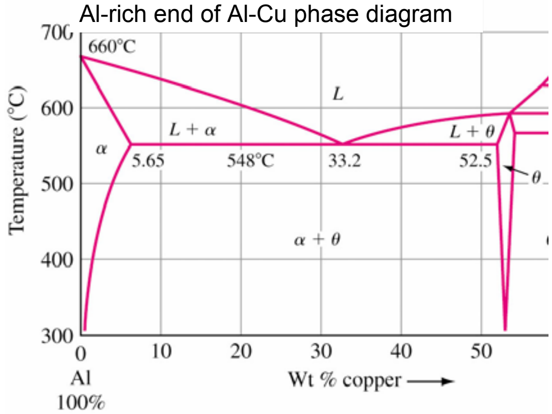




1. Initially only few clusters of segregated atoms (precipitate zones) are formed
2. Optimum size and distribution of precipitates is necessary for the best strength properties

Aging of Al – 4% Cu Alloy

Al-rich end of Al-Cu phase diagram



1. Solution heat treatment at ~515^oC
2. Quenching to RT
3. Aging at 130-190^oC

During the aging 5 sequential phases can be identified:

1. Supersaturated s. solution, α
2. Coherently precipitated Cu atoms
3. Tetragonal region precipitates aligned along with the {100} of the matrix
4. incoherent precipitate (has the structure different from the matrix)
5. θ ($CuAl_2$) phase

9.6 Copper Alloys

Parent metal Cu:

+ good corrosion resistance (positive electrochemical potential, low chemical reactivity)

+ high electrical conduction (Ag > Cu >…) and high thermal conductivity

- medium tensile strength ⇒ can be alloyed

- high price…

Copper ores: CuS, (Cu, Fe)S, Cu metal

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$ tough-pitch copper (>98% Cu)

Further purification ⇒ electrolytic tough-pitch copper (>99.95% Cu, O 0.04%)

Even high purity - some issues…

O forms Cu_2O, when Cu is cast

$Cu_2O + H_2$ (dissolved in Cu) ⇒ $2Cu + H_2O$ (steam) brittle!

$5\ Cu_2O + 2\ P \Rightarrow 10\ Cu + P_2O_5$ not brittle

casting under reduced atmosphere ⇒ *oxygen-free high-conductivity (OFHC) Cu*

Copper Alloys

Cu – Zn alloys, brasses (phase diagram, Figure 8.27)

Substitutional s. s. solution of Zn (<35%) in Cu (*fcc*) – α phase

High Zn content – ordered *bcc* β phase

Strength: Cu 220Pa; 70Cu_30Zn – 325MPa;

s. steel 550MPa

Cu – Sn bronzes or Phosphorous bronzes

1-10% Sn (solid solution strengthen)

Stronger compared to brass, better corrosion resistance

Cu – Be alloys: 0.6-2% Be, 0.2-2.5% Co

Strength is high as 1463MPa ⇒ tools, requiring high hardness

- high cost

Table 9.11: typical mechanical properties and applications

9.9 Mg alloys

Parent metal Mg *(hcp):*

+ very light (1.74 g/cm^3) $\Rightarrow$ aerospace applications

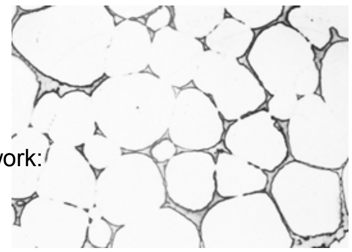
- difficult to cast ($2Mg + O_2 = 2MgO$), cover fluxes must be used
- low melting temperature
- high cost
- poor resistance to creep, fatigue, and wear
- low strength

Major alloying elements: Al, Zn, Mn, rare earth elements

Precipitation hardening (alloys with Al):
$Mg_{17}Al_{12}$ precipitates, age-hardening

Th, Zr (form precipitates in Mg): high T strengths

Mg_9Ce: a rigid grain boundary network:



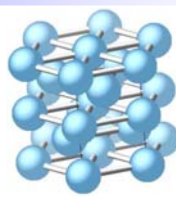
difficult to cold-work Mg alloys as they have an *hcp* crystal structure (restricted slip systems)

Metallic Ti

Parent metal Ti:

+ relatively light (4.7 g/cm^3) $\Rightarrow$ aerospace
+ superior corrosion resistance (O, Cl)
+ high strength (99.9% Ti – 662MPa)

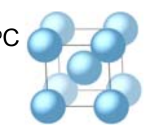
- relatively high price (difficult to extract in the pure state from its compounds, reactions with O, N, C, Fe)



RT, *hcp*

α phase

883^{o}C $\Rightarrow$



bcc

β

Ti ores: $TiFeO_3$ (ilmenite), TiO_2

Kroll method:

$2TiFeO_3 + 7Cl_2 + 6C$ (900°C) $\rightarrow 2TiCl_4 + 2FeCl_3 + 6CO$

$FeCl_3$ and $TiCl_4$ separated by fractional distillation

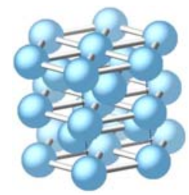
$TiCl_4 + 2Mg$ (1100°C) $\rightarrow 2MgCl_2 + Ti$

Ti separation by HCl/H_2O mixture $\Rightarrow$Ti sponge

Ti Alloys

Al and O are α phase stabilizing elements for Ti

•Ti-6Al-4V : important Ti alloy, combines high strength with workability; reduced density, ductility

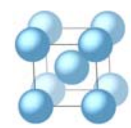


RT, *hcp*

α phase

V and Mo are β phase stabilizing elements for Ti

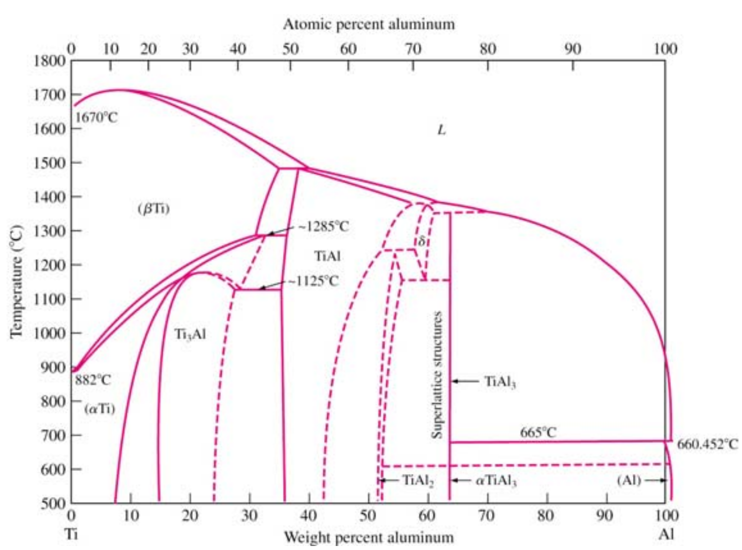
Applications:
• chemical and marine applications,
• aircraft airframe and engine parts,
• weldable forgings and sheet metal parts



bcc

β

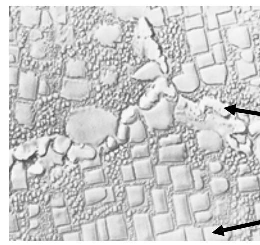
Ti-Al phase diagram



Ni Alloys

Parent metal Ni:

+ high density (8.9 g/cm^3)
+ exceptional corrosion resistance
+ no oxidation at high temperature
- high price



• Monel alloy: 66 Ni – 32 Cu (552MPa)

• Monel K500: 66 Ni – 30Cu – 2.7 Al- 0.6 Ti (1035 MPa)

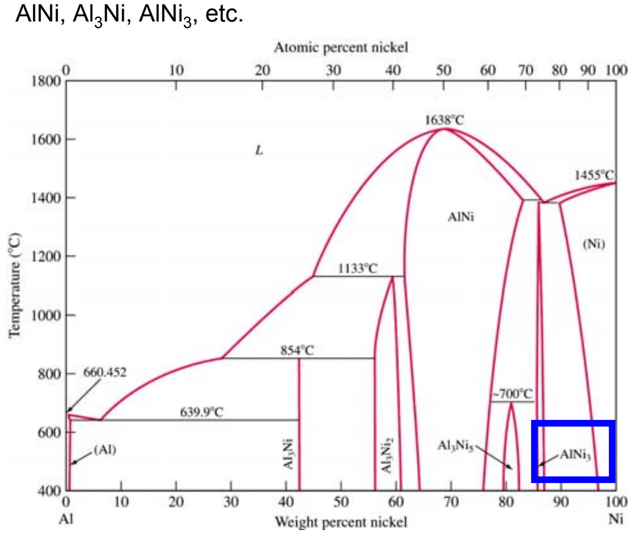
(Precipitation strengthening – Ni_3Al, Ni_3Ti)

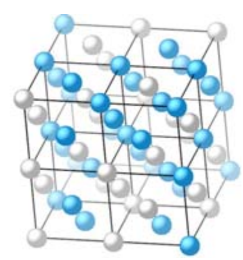
• Ni-base “superalloys”: 50 Ni – 20 Cr – 20 Co – 4Al – 4 Ti (Ni_3Al, Ni_3Ti) - C exceptional in their ability to withstand high T and high oxidation conditions without experiencing significant creep

9.10 Intermetallic

Stoichiometric compounds of metallic elements

AlNi, Al_3Ni, $AlNi_3$, etc.





• high hardness

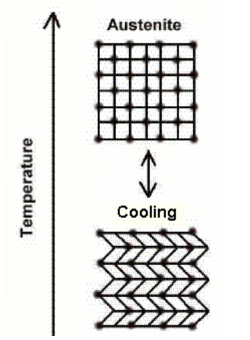
• brittle

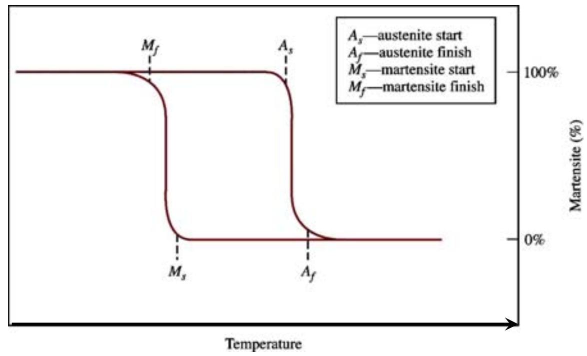
• Al forms Al_2O_3 layer

9.11 Shape-Memory Alloys (SMA)

Shape-Memory Alloys: metal alloys that recover a previously defined shape when subjected to an appropriate heat treatment process

- super elasticity: twinned martensite phase is easy to deform by stress (propagation of the twin boundary)
- shape-memory effects





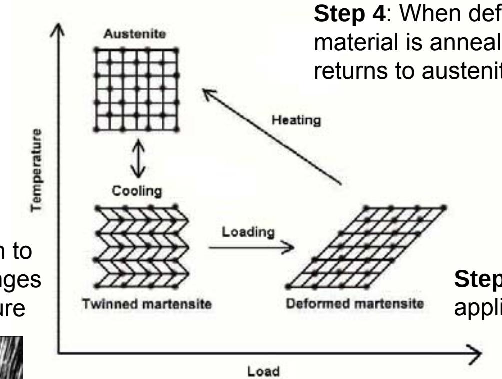
Microstructure change in SMA

Step 1: anneal 500-800°C to impart the desired shape (parent structure)

Step 4: When deformed material is annealed, it returns to austenite structure

Step 2: cool down to RT structure changes to sheared structure

Step 3: stress is applied




(c)

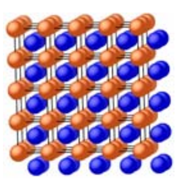
Applications of SMA

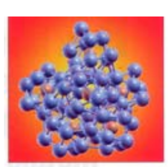
Ex.: Ni (49%)-Ti (51%) (nitinol), Au-Cd, Cu-Zn-Al-Ni
• good mechanical properties: strong
• corrosion resistant
• bio-compatible

1. Aircraft Maneuverability
2. Surgical tools
3. Robotic Muscles

9.12 Bulk Metallic Glasses (BMG)

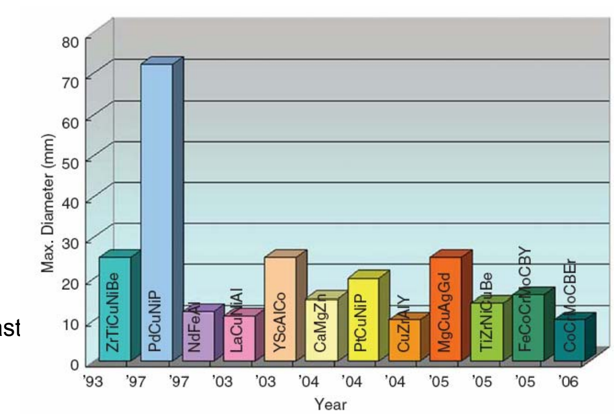
Metals with a noncrystalline structure (also called glassy metals)





No pure metals and few metallic alloys are natural glass-formers

Critical size of BMG: the max possible value of the min dimension



MRS bulletin, August 2007, P.611

Initial idea: extremely fast quenching (10^5 K/s)

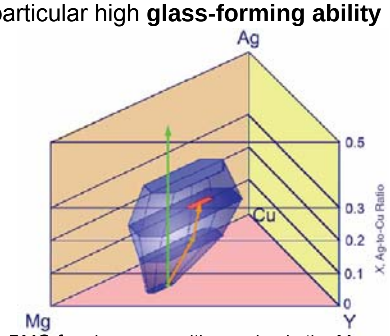
Challenging…

Thermodynamic and kinetic factors

Some alloy compositions may exhibit particular high **glass-forming ability**

<u>BMG are more likely to have :</u>

- 3-5 components
- with large atomic mismatch
- composition close to eutectic
- be densely packed



BMG-forming composition region in the Mg-(Cu,Ag)-Y system. Within the blue region, the critical diameter of the glasses exceeds 8 mm

- low enthalpy and entropy ⇒ low thermodynamic driving force for crystallization
- low atomic mobility associated with viscosity
- viscosity is high and relatively weak T dependent

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Structure of glassy metals

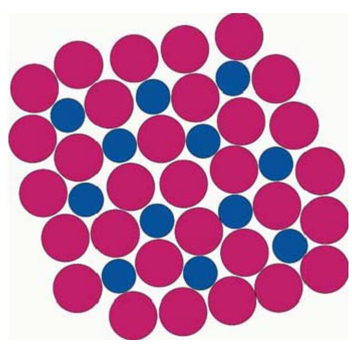
Short-range order (SRO) develops over the first couple of coordination shells (<0.5 nm)

Medium – range order (MRO) may extend to beyond ~ 1nm

How atoms pack in metallic glasses?

From experiments: dense packing is characteristic; microscopic free volume can be unevenly distributed

1. Efficiently packed solute-centered quasi-equivalent clusters organized with ordered packing over
2. Overlapping NN clusters that share the same solvent atoms
3. No orientation order between clusters, so that solvent atoms are randomly packed



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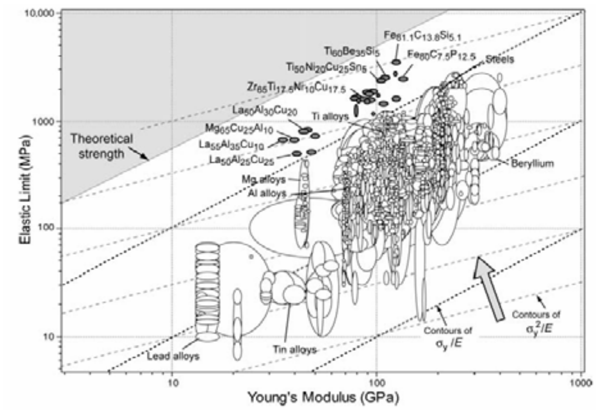
Mechanical Behaviour

Heterogeneous Deformation: in the absence of dislocation–mediated crystallographic slip, deformation in BMG occurs in thin shear bands

- local heating and nanocrystal growth during shear deformation

Mechanical Strength: record yield strength Co-Fe-Ta-B-Mo 5.5GPa



Applications of BMG

Magnetic applications

• magnetic shielding sheets

Chemical

• components in the fuel cells

• diagrams for pressure sensors

Structural Materials

• sport equipment (golf clubs, tennis rackets, etc.)

• precision gears for micromotors

9.13 Medical and orthopedic applications of metals

Specific replacement of damaged or dysfunctional tissue

Ex: orthopedic applications (all or part of the bone or joint reinforced)

Biometals: metal alloys that
- Replace damaged biological tissues
- Restore function
- Constantly or intermittently in contact with body fluids

1. Primary characteristic of a biometal is **biocompartibility**

- chemical stability
- corrosion resistance
- noncarcinogenic
- nontoxic (Cu, Co, Ni: toxic)

Ti, Zr, Pt

S.s. 316L

Co – Cr - Mo

Ti and alloys

2. Be able to cycle under load in the highly corrosive environment (~10^6 cycles)

Summary

- **Alloy** is homogeneous hybrid of 2 or more elements, at least one of which is a metal and has metallic properties
- Fe – Fe_3C phase diagram
  - identify phases
  - invariant reactions
  - formation of martensite phase (microstructure and mechanical properties)
  - steel tempering
- Precipitation hardening mechanism

- Superalloys
- Shape-memory alloys
- Bulk glassy metals

Problems

9.1 Define the following phases that exist in the Fe-Fe3C phase diagram: (*a*) austenite, (*b*) ferrite, (*c*) cementite, (*d*) ferrite.

9.2 Write the reactions for the three invariant reactions that take place in the Fe-Fe3C phase diagram.

9.3 Describe the structural changes that take place when a plain-carbon eutectoid steel is slowly cooled from the austenitic region just above the eutectoid temperature.

9.4 A 0.25 percent C hypoeutectoid plain-carbon steel is slowly cooled from 950°C to a temperature just slightly *below* 723°C. (*a*) Calculate the weight percent proeutectoid ferrite in the steel.

(*b*) Calculate the weight percent eutectoid ferrite and weight percent eutectoid cementite in the steel.

9.5 A 1.10 percent C hypereutectoid plain-carbon steel is slowly cooled from 900°C to a temperature just slightly *below* 723°C. (*a*) Calculate the weight percent proeutectoid cementite present in the steel; (*b*) Calculate the weight percent eutectoid cementite and the weight percent eutectoid ferrite present in the steel.

9.6 What are the advantages of martempering? What type of microstructure is produced after tempering a martempered steel?

9.7 What are the three basic heat-treatment steps to strengthen a precipitation-hardenable alloy?

9.8 What type of surface film protects stainless steels?

9.9 In what respect are the nickel-base superalloys “super”? What are the three main phases present in nickel-base superalloys?

9.10 Describe structural changes in shape memory alloys.