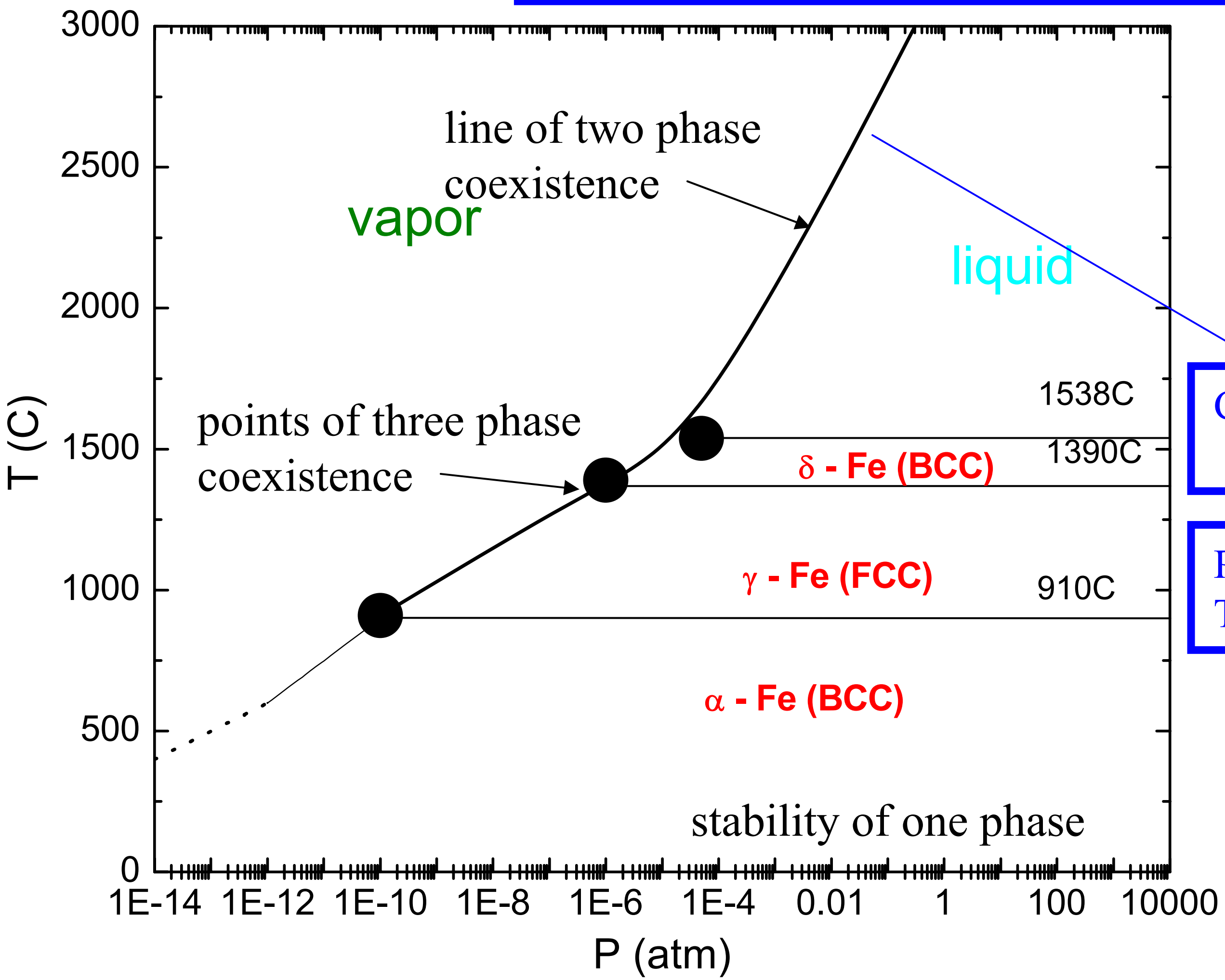
Phase Diagrams

- Starting point and necessary ingredient in materials synthesis
- Show phases that are stable under equilibrium conditions for some values of parameter range – usually (x,T), but also pressure, magnetic field
- Binary alloy, ternary alloy phase diagrams
- Solid, liquid, vapor
- Often estimates and sometimes unexplored, even binary alloy

Phase Diagrams

equilibrium T-P phase diagram of Fe



There are:

3 stable solid phases

Liquid phase

Vapor phase

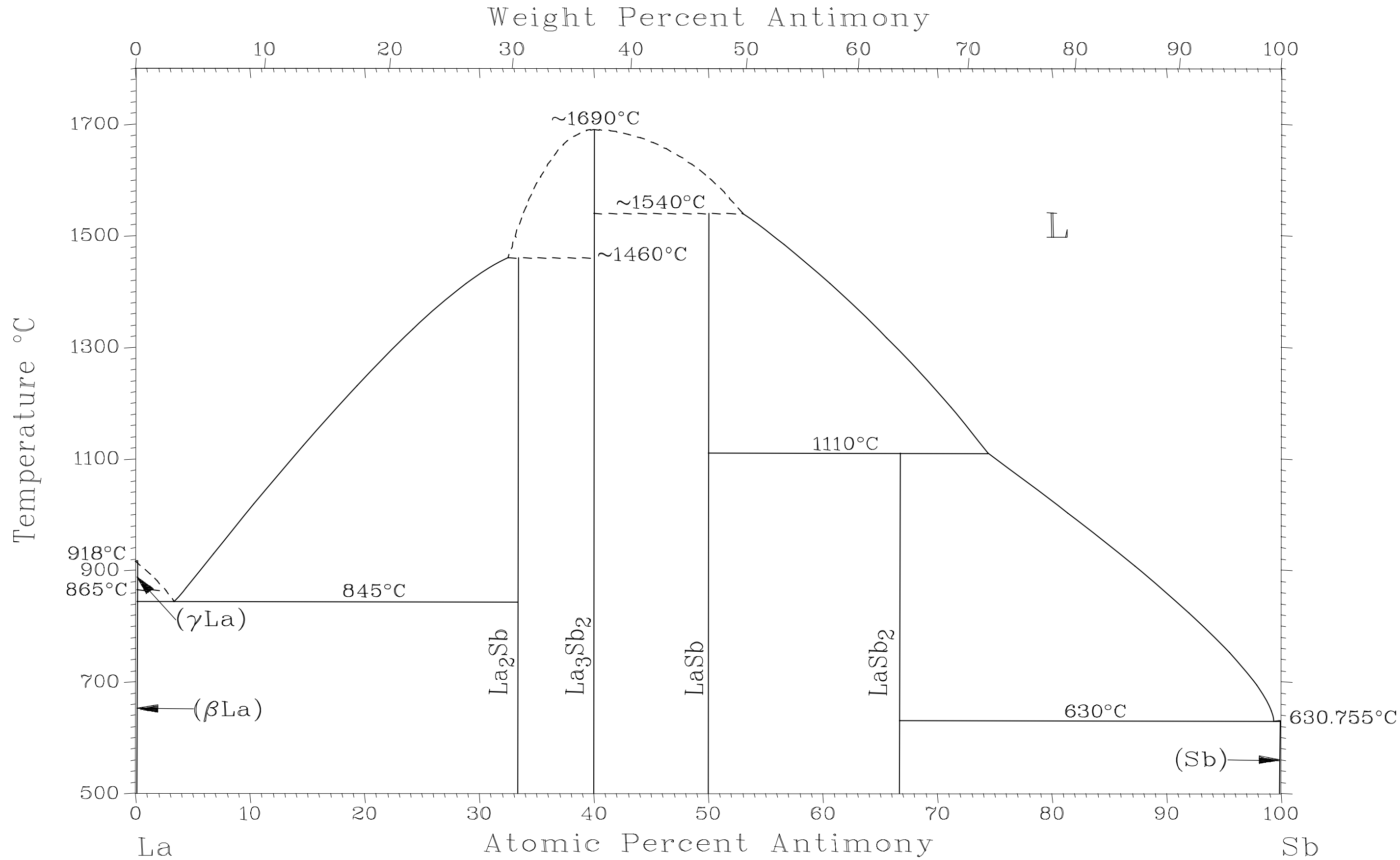
Coexistence of phase 1 and 2:
$G_1 = G_2$

P_{eq} is pressure corresponding
To vaporization line

$\Delta H_m = T_m \Delta S_m$ (melting)

- Phase transitions occur by varying P, T (or x, T as it is usual) – by crossing the line at the diagram
- P – T phase diagram: Since $G_1=G_2$, $\Delta G = 0 = VdP - SdT$ ⟶ $dP/dT\ (slope) = \Delta S/\Delta V = \Delta H/T\Delta V$

Phase Diagram of Binary System



InAs

GaAs

Pseudobinary possible

- Starting point in synthesis
- Estimates
- Extensive use in crystal growth
- Flux method

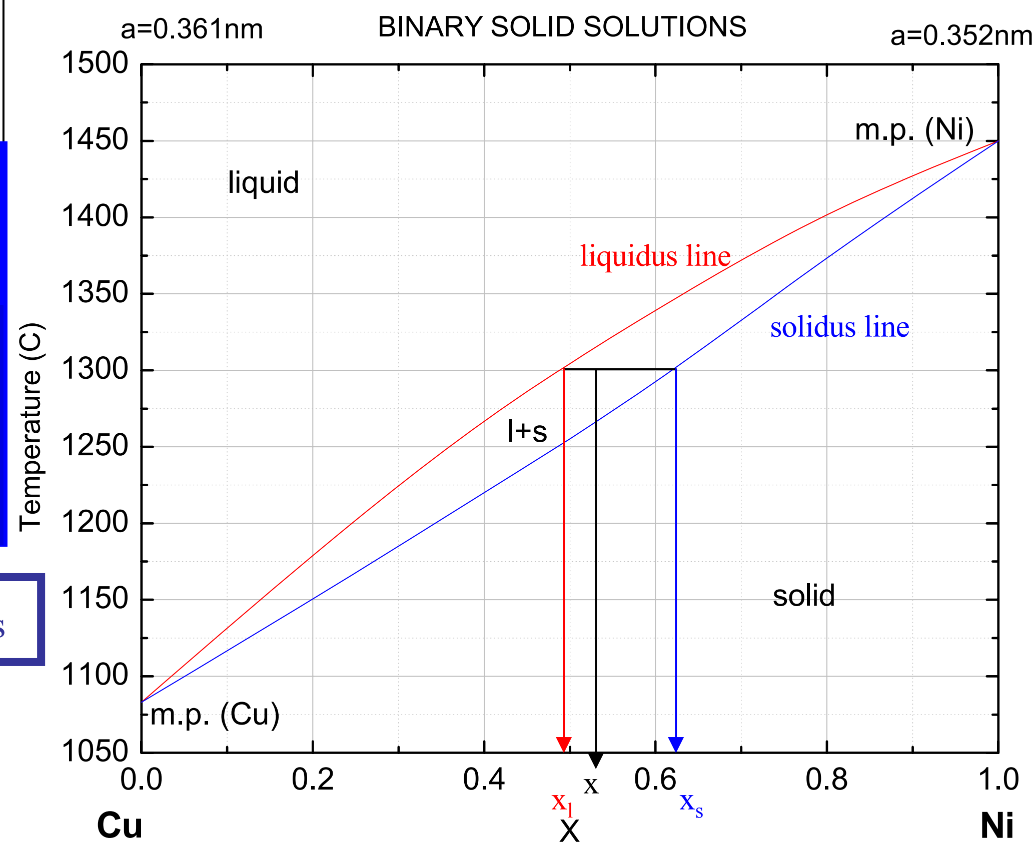
Phase Diagrams

Binary solid solution characteristics:

1. Two elements soluble in each other for all x
2. Atoms can subsitute each other on the lattice sites
3. Same crystal structure for all x
4. Close match in lattice parameters ~ up to 15%
5. Should not form compounds with each other ~ same electronegativity
6. Should have the same valence

Hume – Rothery rules

	Cu	Ni
SG	Fm-3m	Fm-3m
A(Å)	3.61	3.52
Conf	3d104s1	3d84s2
Valence	2,1	2,3
Ion. V(ev)	7.72	7.63



- **Two phase region**: $x_l \neq x_s$. *G=G (T,P.x)*. Solid **s** phase always rich in ***higher melting point element*** Ni relative to overall alloy composition x. Liquid phase always rich in Cu atoms. In the two phase region $Cu_{1-x}Ni_x$ alloy:

number of Ni moles solid ← → number of Ni moles liquid

$$n_s x_s + n_l x_l = (n_s + n_l)x = nx$$

x-Ni mole concentration

total number of Ni moles

Solving for relative mole fraction:

$$\frac{n_s}{n} = \frac{x - x_l}{x_s - x_l}; \frac{n_l}{n} = \frac{x_s - x}{x_s - x_l}$$

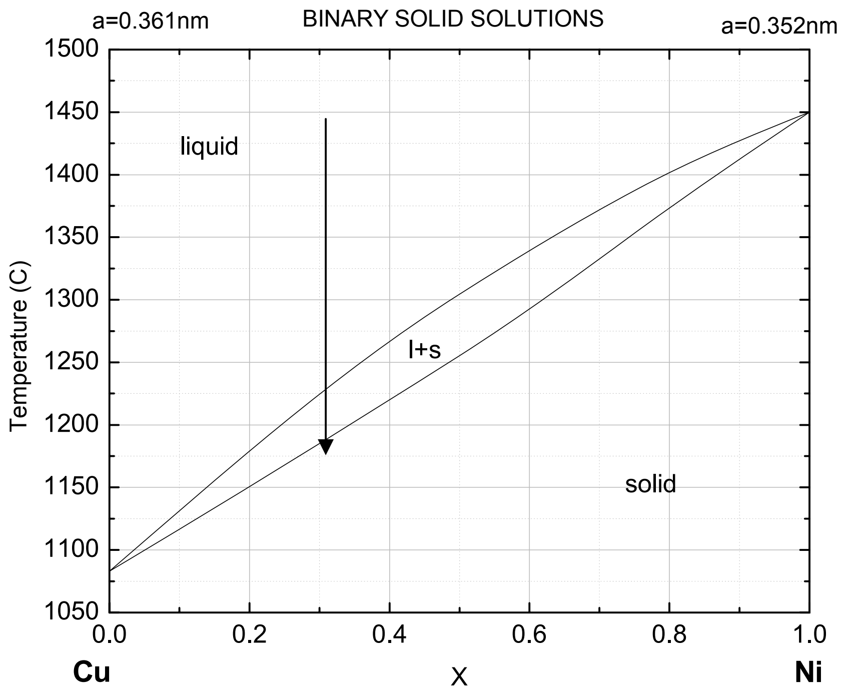
→ Lever Laws

Phase Diagrams

In practice phase diagram is inhomogeneous. Consider cooling from 1450 ºC.

When **l+s** region is entered from **l** phase, solidification of **s** phase begins. Its composition is different from liquid. First to solidify are local clusters that contain more Ni. As solidification grows there will be less Ni and More Cu, so its composition will be different from initial.

Composition gradients are possible. Microstructure of solid alloy will consist of microcrystallites. Smaller crystallites correspond to higher cooling rates



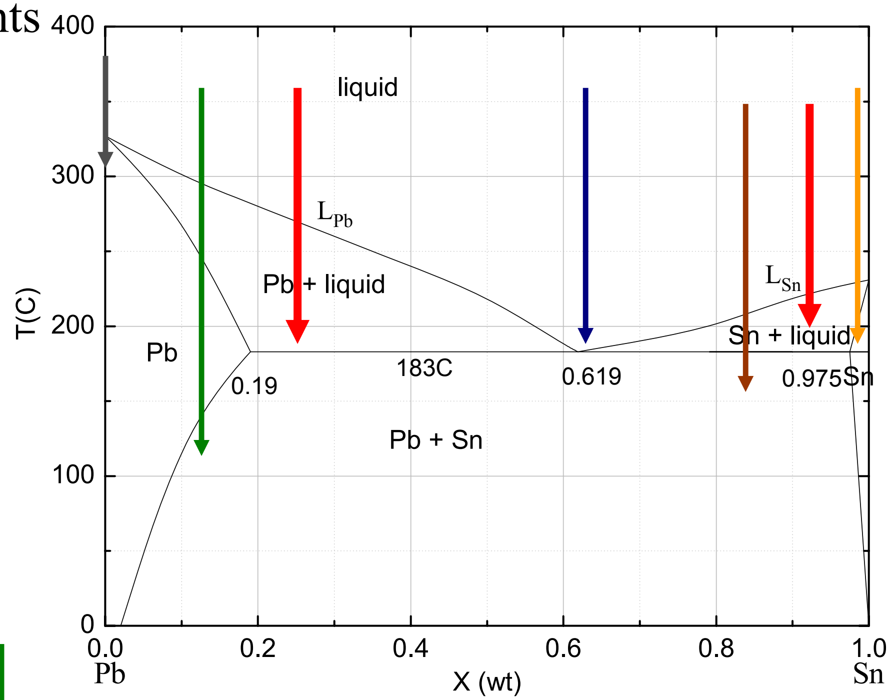
Rapid solidification: crystalline size is extremely small ~ few atoms – solids amorphous.

- In l and **s** phase only alloys with any fixed x are possible – two degrees of freedom (x,l)
- In **s+l** region for any fixed T there are only 2 values of x: x_l *and* x_s – one degree of freedom T
- A, B *completely miscible* if there is no preference for AA, AB or BB type of bonds and the energy of AB bond is the average of AA and BB: $E(A\text{-}B) = \langle E\rangle = [E(AA)\text{-}E(BB)]/2$
- Then $\Delta H_{mix} = 0$ so $\Delta G_{mix} = - T\Delta S_{mix}$. *Entropy always randomizes the bonding*.
- In reality, A and B are not identical $E(AB) \neq \langle E\rangle$, ***so the lower the T the weaker is S and there is less miscibility***
- If $E(A\text{-}B) > \langle E\rangle \longrightarrow$ compounds are formed; if $E(A\text{-}B) < \langle E\rangle$ there is a phase separation

Binary Eutectic Alloys

Consider chemicaly or physically different elements
$\partial G/\partial x$ has several minima

Eutectic point
Lowest solidification point in the alloy system
Liquid phase undergoes isothermal reversible transformation into heterogeneous mixture of two solid phases.



Make a sample of Pb

Make a sample of Pb – rich $Pb_{1-x}Sn_x$ alloy

Make a sample of Sn – rich $Pb_{1-x}Sn_x$ alloy

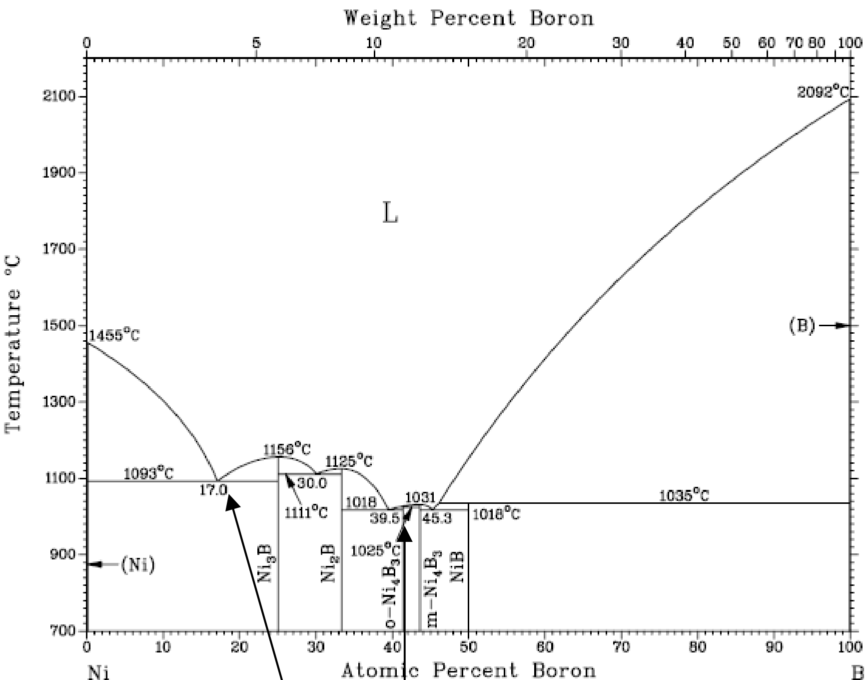
Make a sample of Sn

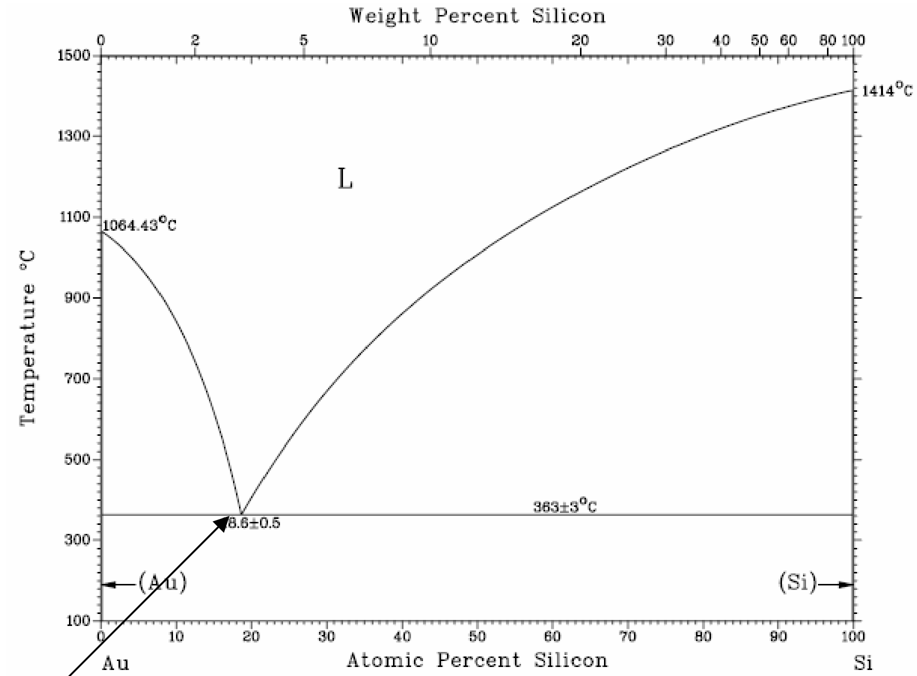
Can we make **crystals** of Pb and Sn?

Crystals are formed when liqiudus line is crossed at point L_{Pb} and L_{Sn}.
They grow in number and size until eutectic line.

Binary Phase Diagrams

can be rather complex

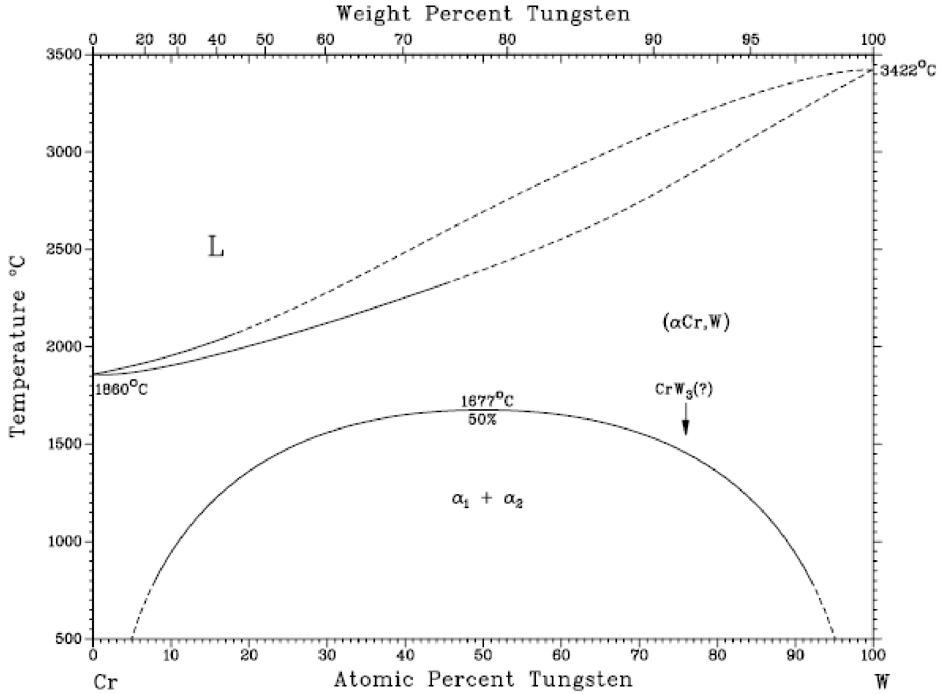




- ❑ Eutectic lines can be much lower than melting points of end constituents
- ❑ Eutectic point: liquid borders directly on solid phase
- ❑ Usually formed with elements with different bonding preferences: covalent (Si), metallic (Au)
- ❑ Extensive use in flux crystal growth

Spinoidal Decomposition

problem in crystal growth



- ❑ There is solubility or miscibility gap for some (x,T).

- ❑ Two new phases have same crystal structures but different compositions than single phase alloy above miscibility gap

- ❑ Within spinoidal region phase separation can occur spontaneously as T is lowered without nucleation barrier. Small fluctuations of *x* lower *G*. Controlled by diffusion

Melting

Amplitude of atomic vibrations around equilibrium positions increase due to increased T.
As a consequence, there is breakdown of long range order.
Changes in bonding also introduce changes in short range order,
Change in arrangement and number of NN's
Initiation of melting controlled by surfaces, grain boundaries, dislocations
Melting temperature determined by bonding strength (think In and B…)

- $G_{solid}(T,P,V,x) = G_{liquid}(T,P,V,X)$ at T_m, but $S = -(\partial G/\partial T)_P$, $V = -(\partial G/\partial P)_T$ and H change discontinuously (discontinuity in the first derivative - *first order phase transition*)
- At T_m $(S \longrightarrow L)$ entropy increases by ΔS_m and $\Delta H_m = T_m \Delta S_m \neq 0$ (latent heat is released) since liquid phase has higher internal energy (disorder) but lower cohesive energy
- Melting occurs when the amplitudes of thermal vibrations of the atoms exceed a critical fraction f_c of NN distance d: $(\langle u^2 \rangle)^{1/2} = f_c d$
- Assume lattice potential harmonic, then:

$$\langle E \rangle = C(f_c d)^2/2 \qquad \text{where } C = m\omega^2$$

- Total vibrational energy:

$$\langle E \rangle = m\omega^2 (f_c d)^2/2$$

- Since $T_m > \theta_D$ one can use classical result for a 3D harmonic oscillator $\langle E \rangle = 3k_B T_m$

$$T_m = \frac{m\omega^2 (fcd)^2}{6k_B} = \frac{mk_B \theta_D^2 (fcd)^2}{6\hbar^2} \qquad (\hbar\omega = k_B T)$$

Critical amplitude for crystals is around 8-9 % of NN distance d

Melting temperature

Melting

- Generalization of Lindemann criterion for **disordered materials** in addition to thermal: crystalline to amorphous state transition will occur below T_m when sum of thermal and static disorder reaches ***$f_c d$***:

atomic displacements

$$(\langle u^2 \rangle_{th})^{1/2} + (\langle u^2 \rangle_{st})^{1/2} = f_c d$$

- Mechanism assumes that melting occurs homogeneously in the bulk of solid, but there are other approaches as well.
- More accurate approaches: *melting occurs at the surface*, then propagates into the bulk of crystal. Propagation velocity increases with temperature.
- ***What may occur during melting – solidification process is supercooling***: formation of the critical nucleus of the solid as the liquid is cooled below meltin point $T_{m.}$ That nucleus will survive thermal fluctuations and will continue growing.
- Surface can melt at T below the bulk, has lower θ_D. Surface film wets the solid – vapor interface and its thickness diverges at T_m. Surface will melt if its $F/A=\sigma$

$$\sigma_{sv} > \sigma_{sl} + \sigma_{lv}$$

- ΔH_m (enthalpy change at melting) is only a few % of ΔH_c (cohesive enthalpy), therefore:

considerable amount of cohesion or bonding remains in liquid (important for crystal growth considerations)

Structural Order and Disorder in Solids

Deviation from periodicity
Structural (displacement from equilibrium) and Chemical (substitution)

Found in crystals

- Spatial extent of the ordered regions (crystallites):

polycrystalline	microcrystalline	nanocrystalline	amorphous
~ mm	~ μm	~ nm	less than nm

- **Long range order** – in ordered crystalline solids but also in ordered regions of disordered solids..
- **Intermediate range order** – when order extends to neighboring units beyond local atomic bonding unit (mixed bonding units, for example sp^2, sp^3 and hex rings of C in amorophous C)..
- **Short range order** – arrangements of NN's are the same as in crystalline solids and bonding units are present, however bond lengths and angles are different.

- Composites – multiphase mixtures, usually some alloys in the matrix
- Colloids – aggregates of particles in nm or μm range, shapes depend on growth conditions, crystallinity (retain morphology of the ordered phase)
- Nanoclusters – agregates of particles in nm range – fullerenes C_{60}
- Thin films, multilayers – 2D, interfaces exist
- Quasicrystals – have symmetries not found in crystalline solids (fivefold axes, icosahedral units that cannot fill space when packed together alone, do not have translational symmetry.

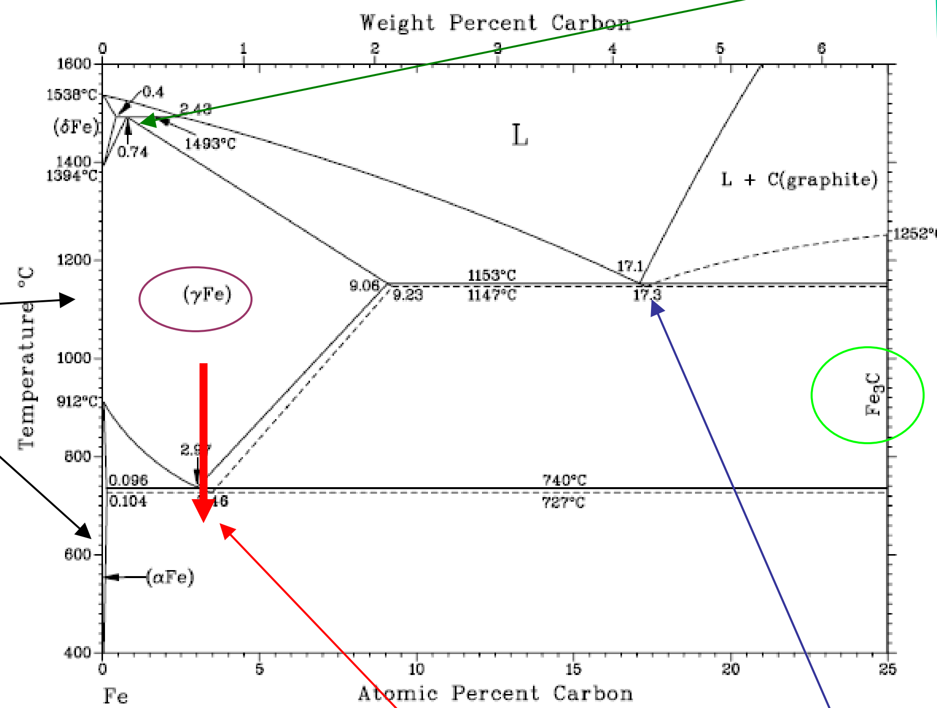
Synthesis of polycrystalline metals - Steels

most important group of metal alloys: mechanical properties

Peritectic
l+s=s (x=const)

- $Fe_{1-x}C_x$ where $0.002 < x < 0.06$ (plain carbon steels), stainless steel up to 20% additional elements: Si, Ni, Mn, Cr, Mo, N…but also imurities such as O_2, S_2
- Ferrite (BCC α – Fe) – low T phase,

  Austenite (FCC γ – Fe) – high T phase
- But equilibrium is between Fe and Fe_3C (cementite)
- Solubility depends on structure. Features of the crystal structure may favor occupation of certain interstitial octahedral sites in the space group (FCC) by extrinsic C or N atoms or substitution of Fe by larger atoms (transition metals).



- Substitution by transition metals may require homogenization by annealing at 1200ºC since larger atoms (non – interstitials) have lower diffusivities than smaller (C,N).
- Austenite – Ferrite phase transition for pure Fe at 912°C, volume increases by 1%
- Austenite coexists with Ferrite and Fe_3C (cementite) on Fe – C phase diagram at eutectioid temperature T_e = 727°C and x = 3.5% (at.).
- Cooling through T_e from austenite (3.5at% C) yields pearlite, composite of ferrite ($Fe_{0.999}C_{0.001}$) and cementitite Fe_3C
- Stainless steels: 13-26 wt% of Cr due to protective layer of Cr_2O_3

Not to be confused with eutectic