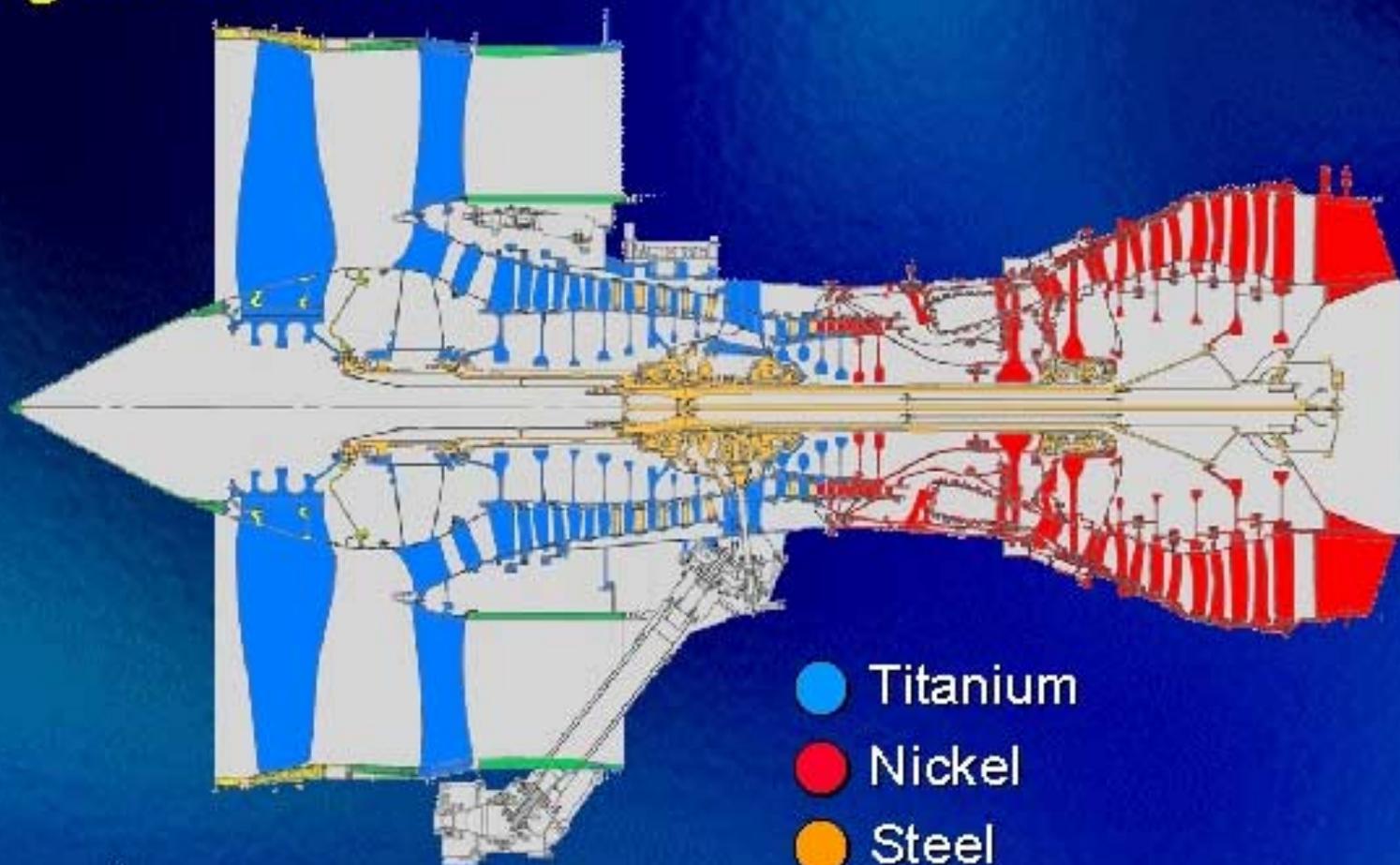


Metals and alloys. Hume-Rothery rules.

- 1. Three types of metals.*
- 2. Alloys. Hume-Rothery rules.*
- 3. Electrical resistance of metallic alloys.*
- 4. Applications of metallic alloys.*
- 5. Steels. Super alloys.*
- 6. Electromigration in thin wires.*

Engine Materials



- Titanium
- Nickel
- Steel
- Aluminium
- Composites



Rolls-Royce

Three types of metals

Metals share common features that define them as a separate class of materials:

- *Good thermal and electrical conductors (Why?).*
- *Electrical resistance increases with temperature (Why?).*
- *Specific heat grows linearly with temperature at low (Why?). temperatures.*
- *Good reflectivity in infrared and, for some metals, in visible light (Why?).*
- *High molar densities and structures with large number of nearest neighbors(Why?).*

Properties of metals are largely defines by their electron structure.

For sp-bonded metals assuming one can assume that the macroscopic properties are the energy of electron gas (see lecture notes of the fall semester).

Energy of an electron gas with Fermi energy E_F :

$$U = \frac{3}{5} n E_F = \frac{3}{10} \frac{N \hbar^2}{m} \left(\frac{3\pi^2 N}{V} \right)$$

Pressure of electron gas: $P = - \left(\frac{\partial U}{\partial V} \right)_S$

Bulk modulus: $B = -V \left(\frac{\partial P}{\partial V} \right)_S = -V \left(\frac{\partial^2 U}{\partial V^2} \right)_S = \frac{2nE_F}{3}$

This derivation does not include the attraction force between the lattice and the electrons and coulomb repulsion.

sp-bonded metals follow Sommerfeld model.

Properties of *sp*-Bonded Metals

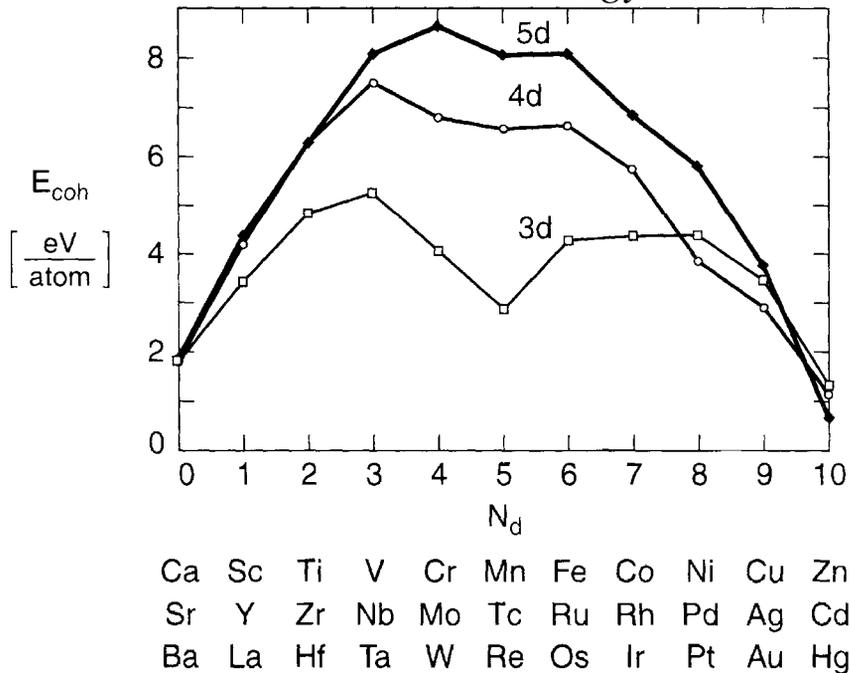
Element	Valence z	Crystal	Cohesive Energy E_{coh} (eV/atom)	Bulk Modulus B (GPa)	Melting Temperature T_m (K)	Debye Temperature Θ_D (K)	Coefficient of Thermal Expansion α (10^{-6} K^{-1})	Cutoff Radius ^a r_c (nm)	Calculated Bulk Modulus ^b B_{th} (GPa)
Li	1	BCC	1.66	11.6	454	352	45	0.070	15
Na	1	BCC	1.13	6.81	371	157	71	0.093	7.5
K	1	BCC	0.94	3.18	337	89	83	0.117	3.4
Rb	1	BCC	0.88	3.14	312	54	88	0.131	2.6
Cs	1	BCC	0.83	2.03	302	40	97	0.146	2.1
Be	2	HCP	3.34	100	1560	1160	12	0.040	170
Mg	2	HCP	1.53	35.4	923	396	26	0.069	47
Ca	2	FCC	1.83	15.2	1115	234	22	0.092	22
Sr	2	FCC	1.70	11.6	1050	147	20	0.102	16
Ba	2	BCC	1.86	10.3	1000	111	19	0.107	14
Al	3	FCC	3.34	72.1	933	423	23	0.059	160
Ga	3	ORT	2.81	56.1	303	317	18	0.063	130
In	3	TET	2.49	41.1	430	109	31	0.072	90
Tl	3	HCP	1.88	35.9	577	—	29	0.076	79
β -Sn	4	TET	3.12	111	505	236	5.3	—	—
Pb	4	FCC	2.04	42.9	601	102	29	—	—
Sb	5	TRIG	2.70	2511	904	150	11	—	—
Bi	5	TRIG	2.17	3054	545	119	13	—	—

*sp-bonded metals are quite different: **Ia** –metals are soft, **IIa** – metals are hard, **IIIa** and **IVa** – metals are soft. Most of these metals are good conductors.*

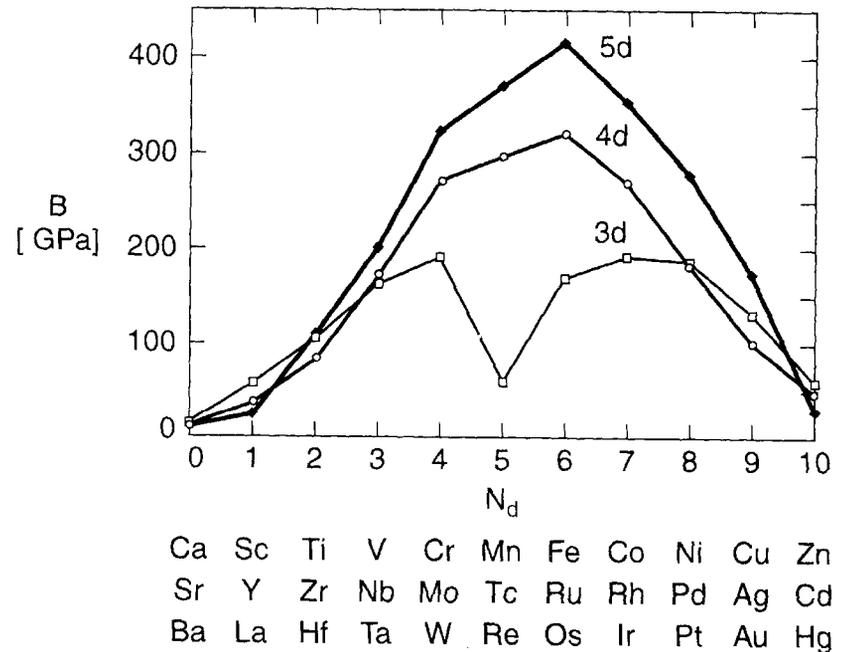
Transition metals.

Properties of transition metals strongly depends on the number of d electrons!

Cohesive energy



Bulk modulus.



Melting temperatures and elastic constant follow the same pattern.

The behavior reflects the strength of the d -orbital interactions.

Rare Earth Metals.

Selected Properties of the Rare Earth Metals

Element	Crystal	E_{coh} (eV/atom)	T_m (K)	Θ_D (K)	n (10^{28} m^{-3})	ρ ($10^{-8} \Omega \cdot \text{m}$)	γ (J/mol·K ²)	m^*/m
La	DHCP	4.4	1191	142	8.0	61	0.010	19
Ce	DHCP	4.3	1071	146	11	74	0.058	137
Pr	DHCP	3.7	1204	85	8.7	70	0.022	45
Nd	DHCP	3.3	1294	159	8.8	64	0.0089	18
Pm	DHCP	2.8	1315	158	8.9	75	0.010	21
Sm	TRIG	2.2	1347	116	9.1	94	0.011	23
Eu	BCC	1.9	1095	127	4.1	90	0.0028	3.4
Gd	HCP	3.6	1586	170	9.1	120	0.01	21
Tb	HCP	3.9	1629	150	9.4	120	0.0091	19
Dy	HCP	2.9	1685	172	9.6	91	0.0093	20
Ho	HCP	3.1	1747	114	9.6	94	0.026	56
Er	HCP	3.1	1802	134	9.8	86	0.013	29
Tm	HCP	2.5	1818	127	10	70	0.020	44
Yb	FCC	1.7	1092	118	4.9	28	0.0029	4.0
Lu	HCP	4.3	1936	210	10	56	0.010	22
Ac	FCC	4.5	1470	124	8.0	—	0.0096	18
Th	FCC	5.9	2028	170	9.1	15	0.0047	10
Pa	BCT	5.7	1845	159	11	18	0.007	17
U	ORTH	5.4	1408	200	14	28	0.011	31
Np	ORTH	4.9	912	121	14	120	0.011	31
Pu	MONO	4.0	913	171	15	150	0.049	143
Am	DHCP	—	1449					
Cm	—	—	1173					
Bk	—	—	1323					
Cf	—	—	1173					
Es	—	—	1133					

f-orbitals are localized and interaction between f-orbitals of different atoms is weak.

Most of the RE metals are trivalent (exception Ce^{4+} , Sm^{2+} , Eu^{2+}).

Most of RE metals are poor electrical conductors due to magnetic scattering (interaction of conducting electrons of with magnetic spin moments f-electrons).

At low temperatures resistivity of RE metals increases with temperature (Kondo effect).

Melting points of RE metals are higher than those of sp-bonded ones but lower than the melting points of transition metals.

Effective electron mass in RE metals is 10-100 times larger than that of a free electron(Why?).

Alloys.

Reminder: An alloy is a phase comprising of one or more components.

There distinguish three of alloys:

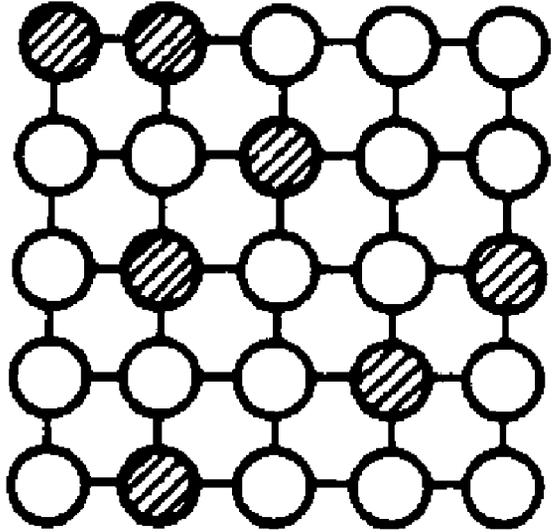
Substitutional: solute substitutes the solvent in the crystal lattice without structural changes.

Interstitial: solute does not occupy the sites in the lattice of the solvent but resides in crystallographic pores.

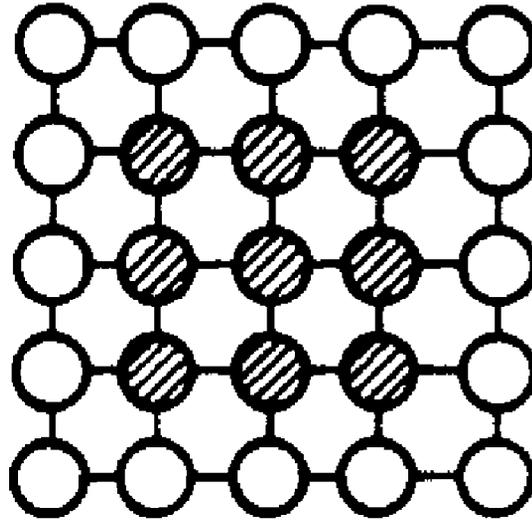
Transformational: A completely new lattice is formed. Usually occurs as a result of intermetallic compound formation.

Substitutional Solid Solution

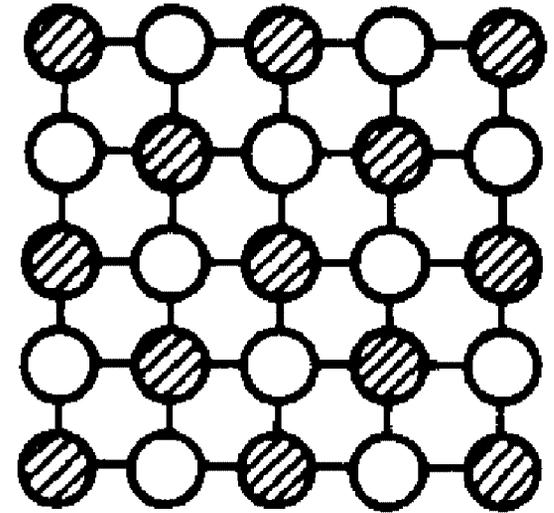
In substitutional solid solution, the arrangement of the solute atoms may be disordered (random) or ordered.



Random



Clustered



Ordered

Some alloy systems exhibit complete solid solubility (e.g. Cu-Ni, Cd-Mg), others show only limited solubility at any temperature.

Several factors determine the limits of solubility. These are expressed as a series of rules often called William Hume-Rothery Rules. These are:

Hume-Rothery Rule 1: Atomic Size Factor (the 15%) Rule.

Extensive substitutional solid solution occurs only if the relative difference between the atomic diameters (radii) of the two species is less than 15%. If the difference > 15%, the solubility is limited. Comparing the atomic radii of solids that form solid solutions, the empirical rule given by Hume-Rothery is given as:

$$\text{Mismatch} = \left(\frac{r_{\text{solute}} - r_{\text{solvent}}}{r_{\text{solvent}}} \right) \times 100 \leq 15\%$$

Hume-Rothery Rule 2: Crystal Structure Rule .

For appreciable solid solubility, the crystal structures of the two elements must be identical.

Hume-Rothery Rule 3: Valency Rule .

A metal will dissolve a metal of higher valency to a greater extent than one of lower valency. The solute and solvent atoms should typically have the same valence in order to achieve maximum solubility.

Hume-Rothery Rule 4: The Electronegativity Rule .

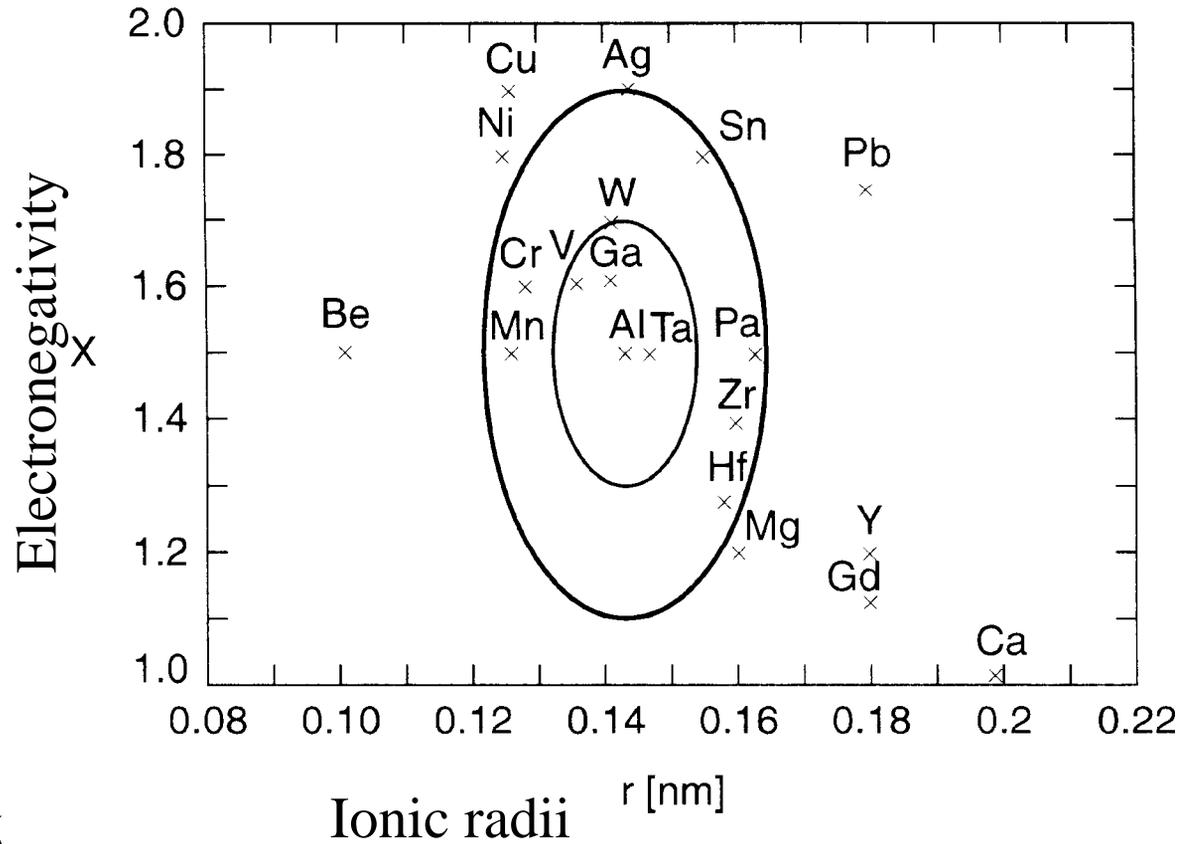
Electronegativity difference close to 0 gives maximum solubility. The more electropositive one element and the more electronegative the other, the greater is the likelihood that they will form an intermetallic compound instead of a substitutional solid solution. The solute and the solvent should lie relatively close in the electrochemical series.

Darken-Gurry maps.

High solubility is expected if the solute atom is within the first ellipse (<0.2 difference in X and <7.5% difference in r) from the solvent.

$$\left(\frac{X - X_A}{0.2}\right)^2 + \left(\frac{r - r_A}{0.075r_A}\right)^2 = 1$$

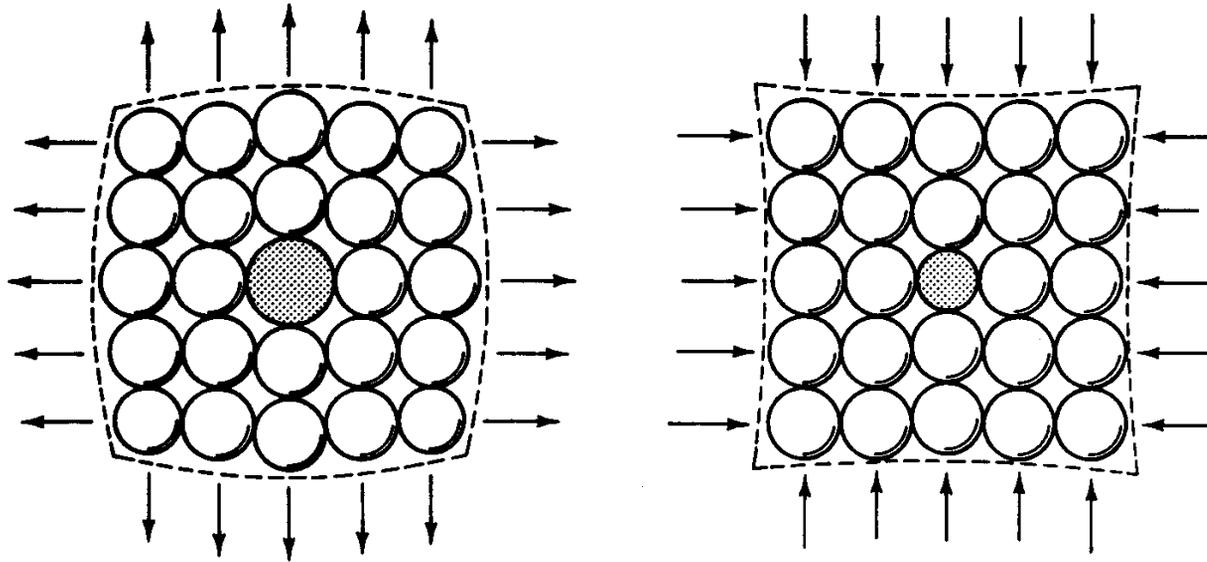
Solubility of at least 5% is expected if the solute atom is within the second ellipse (<0.4 difference in X and <15% difference in r) from the solvent.



Darken-Gurry map for Al

$$\left(\frac{X - X_A}{0.4}\right)^2 + \left(\frac{r - r_A}{0.15r_A}\right)^2 = 1$$

Local stress in substitutional solid solution



Energy associated with the local strain can approximated as:

b is a constant, that depends on crystal crystal structure.

$$S = bB \left(\frac{r_{\text{solvent}} - r_{\text{solute}}}{r_{\text{solvent}}} \right)^2$$

Mixing energy for two components: $\Delta G_M = RT(n_1 \ln n_1 + n_2 \ln n_2 + \chi_{12} n_1 n_2)$

N_1 is molar fraction of solvent; N_2 is molar fraction of solvent; χ is non-ideality constant (for ideal solution =0).

For a solution to exist in a solid phase: $\Delta G_M + n_2 N_A S < 0$

Thus one can explain Hume-Rothery rules by local distortion of the lattice.

Interstitial solid solution

Similar to Hume-Rothery rules can be applied for interstitial solid solutions:

Interstitial solid solutions are formed if

- 1. a solute is smaller than pores in the lattice of a solvent;*
- 2. a solute has approximately the same electronegativity as a solvent.*

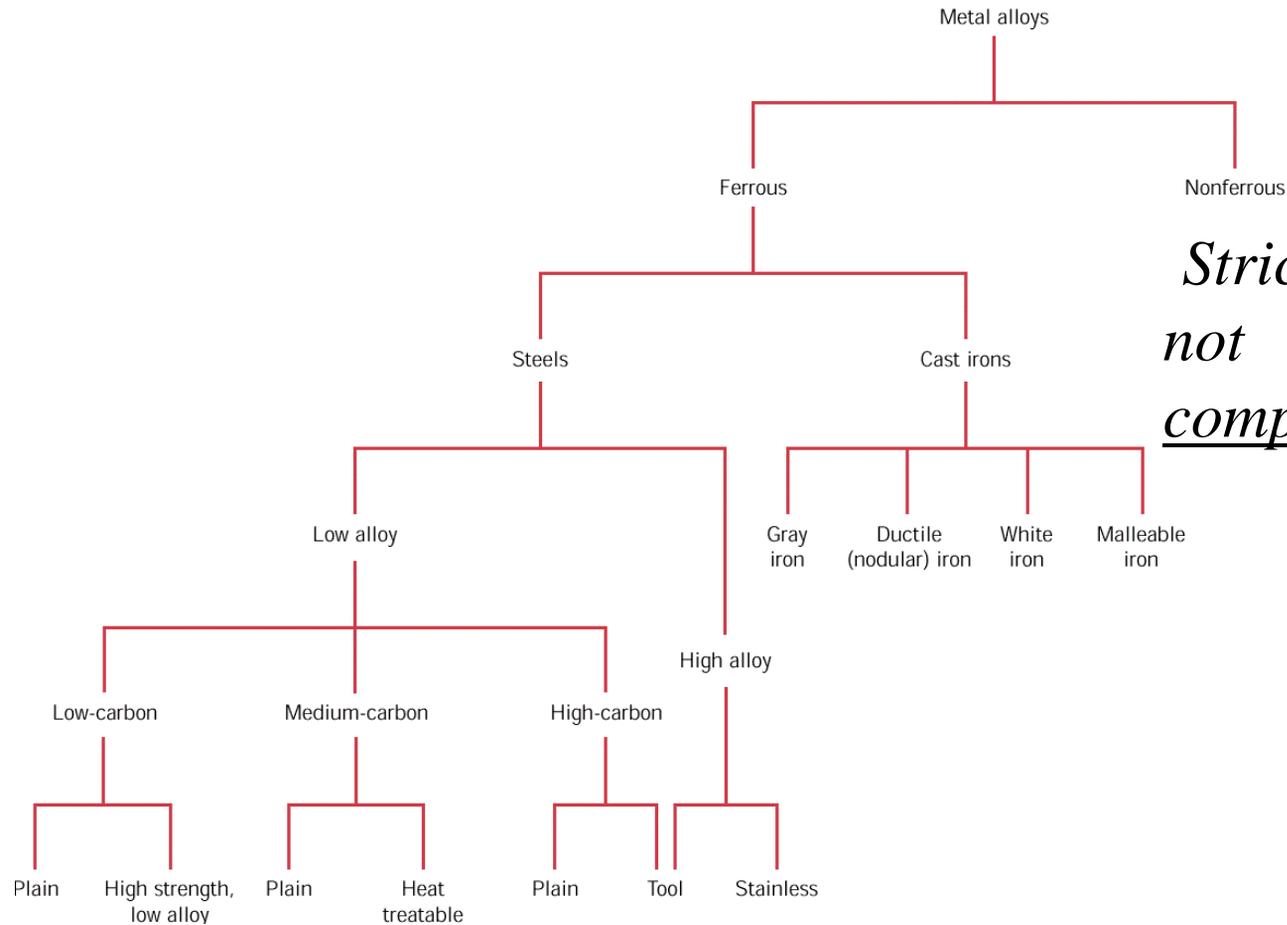
There are very few elements that create ions, small enough to fit in interstitial positions, therefore, appreciable solubility is rare for interstitial solid solutions.

Ions that often may be a solute in solid solutions are: H, Li, Na, B.

Most interstitial solid solutions have a strong tendency to spontaneous ordering(Why?).

Examples of ordered or partially interstitial solid solutions PdH_n , $AlLi_n$, $BeLi$.

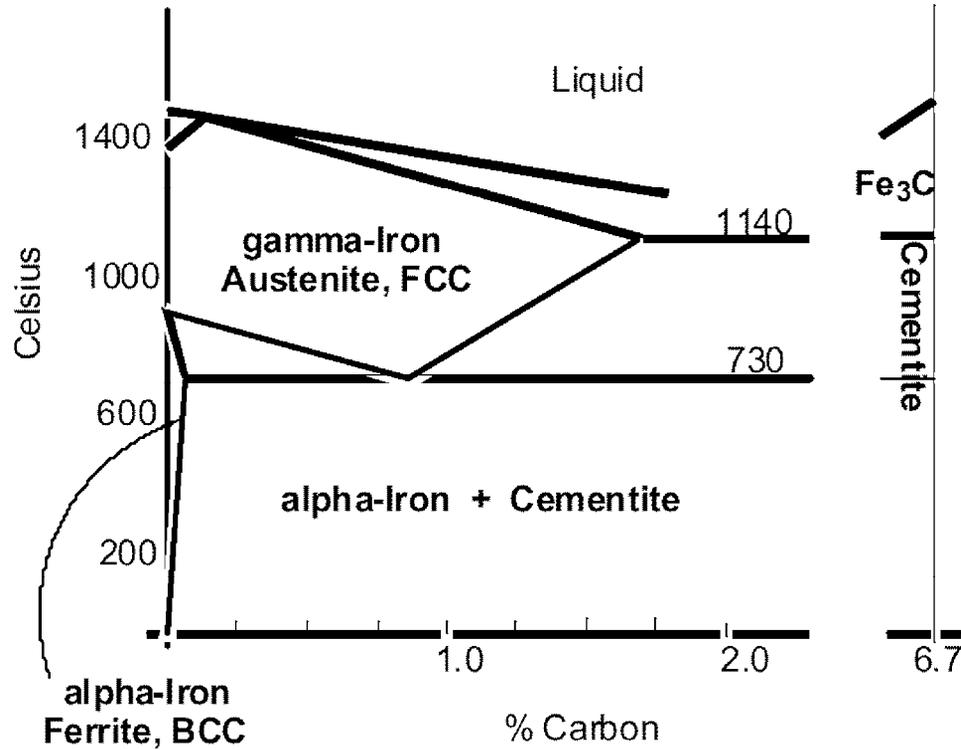
Examples and applications.



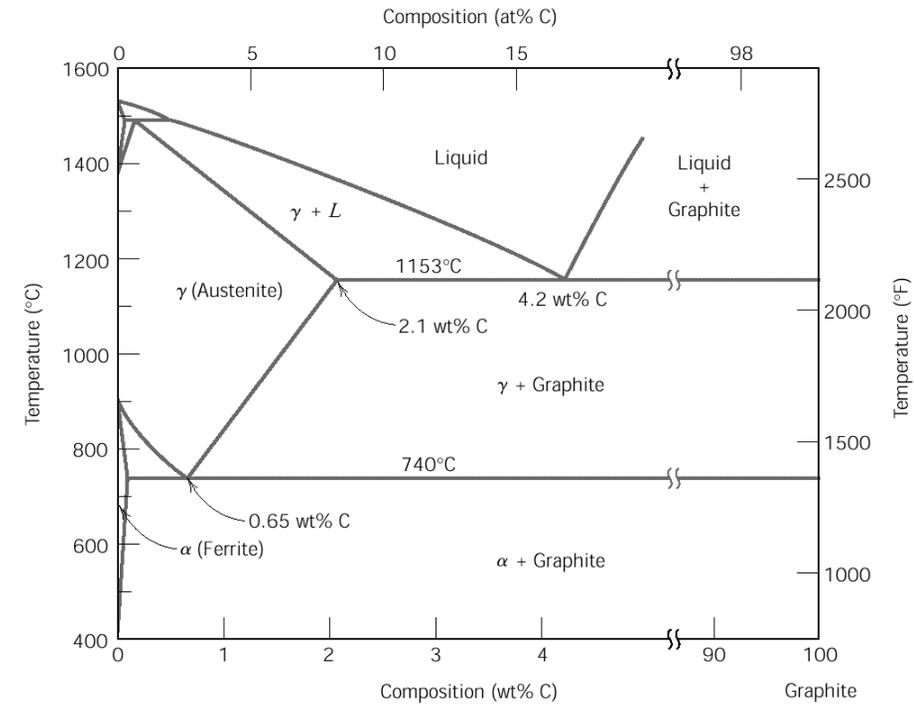
Strictly speaking steel is not an alloy. It is a composite.

Classification scheme for the various alloys.

Phase diagrams.



Pseudo equilibrium



True equilibrium

Most of type of steels are not at equilibrium. Their microstructure is defined by kinetics of phase transformation.

According to kinetics, phase transformations be divided into three categories:

- 1. Diffusion-independent with no change in phase composition or number of phases present*** (e.g. melting, solidification of pure metal, allotropic transformations, recrystallization, etc.).
- 2. Diffusion-dependent with changes in phase compositions and/or number of phases*** (e.g. eutectoid transformations).
- 3. Diffusionless phase transformation*** -produces a metastable phase by cooperative small displacements of all atoms in structure (so-called martensitic transformations).

In contrast other phase transformations, martensitic phase transformation has zero activation energy.

At equilibrium iron may exist in BCC (α -phase, = ferrite low temperature form) and FCC (γ -phase, =austenite, high temperature form).

Martensite forms when austenite is rapidly cooled (quenched) to room temperature.

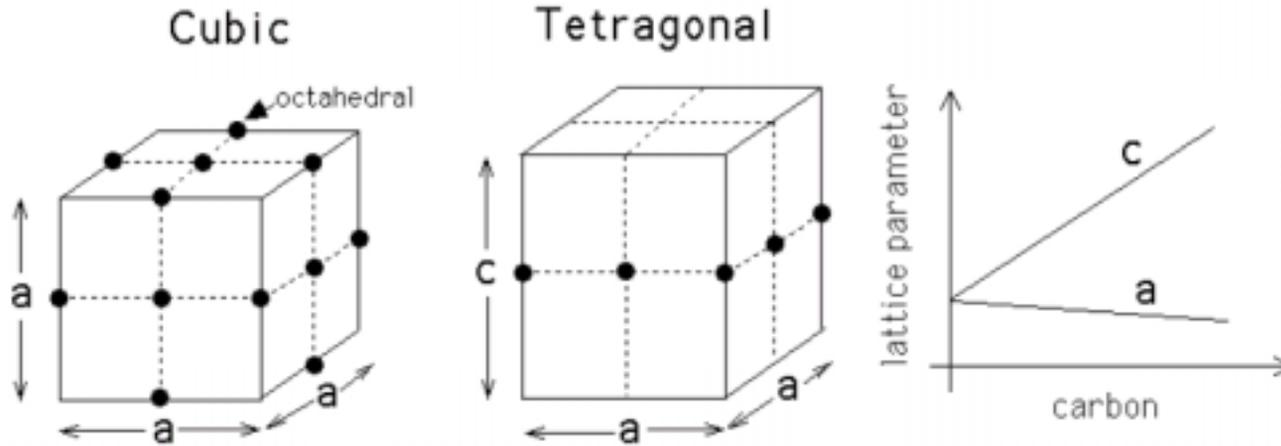
*It forms nearly instantaneously when the required low temperature is reached. The austenite-martensite **does not involve diffusion** and no thermal activation is needed, this is called an **athermal transformation**.*

Each atom displaces a small (sub-atomic) distance to transform FCC, γ -Fe (austenite) to martensite which has a Body Centered Tetragonal (BCT) unit cell (like BCC, but one unit cell axis is longer than the other two).

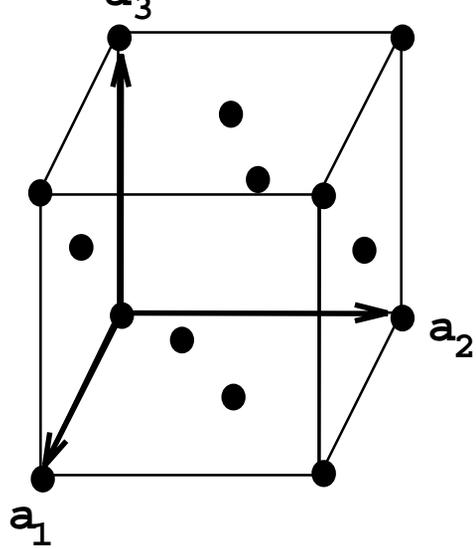
*Martensite is **metastable** -can persist indefinitely at room temperature, but will transform to equilibrium phases on annealing at an elevated temperature.*

Martensite can coexist with other phases and/or microstructures in Fe-C system. Since martensite is metastable non-equilibrium phase, it does not appear in phase Fe-C phase diagram.

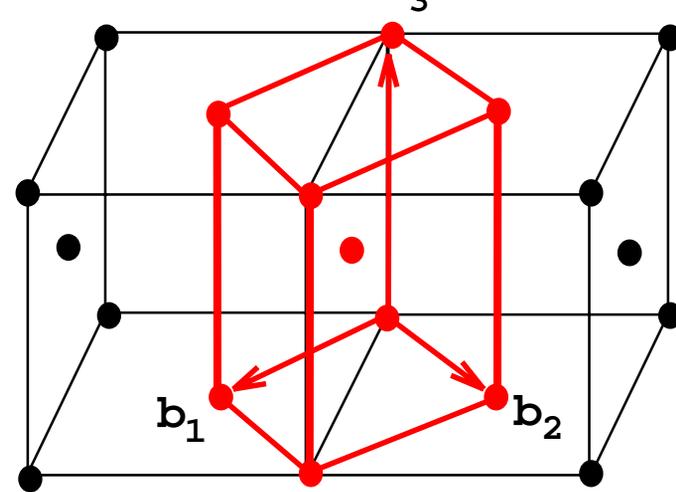
The martensitic transformation begins at a well defined temperature called the martensite-start temperature or M_S . The fraction of martensite increases with the undercooling below M_S .



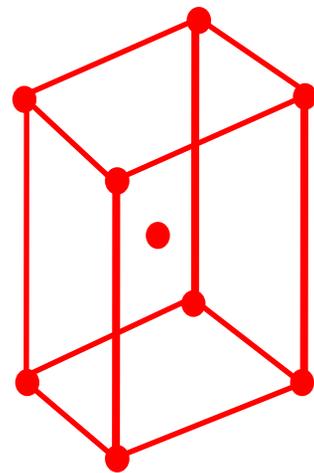
The martensite in steels is supersaturated with carbon. Carbon occupies octahedral interstices in the b.c.c. lattice; these are characterised by three principal axes $a < 0 0 1 >$, $a < 1 1 0 >$ and $a < 1 1 0 >$. There are three sub-lattices of octahedral holes, along directions parallel to the unit cell edges. Each carbon atom causes a tetragonal distortion since the principal axes of the octahedral sites are not equivalent. There is an expansion along $a < 1 0 0 >$ and small contractions along the other two axes. As a consequence, it is favorable for all the carbon atoms to lie on a single sub-lattice of octahedral interstices, giving rise to a body centered tetragonal structure for the martensite



(a)



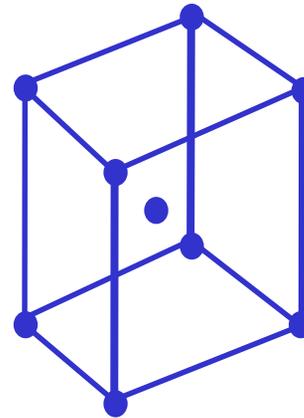
(b)



(c)

Body-centered
tetragonal
austenite

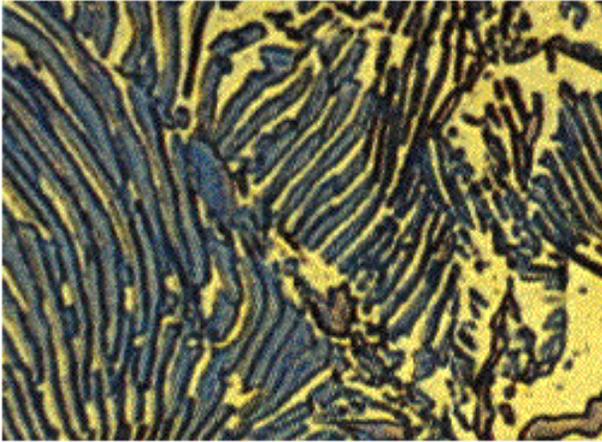
STRAIN



(d)

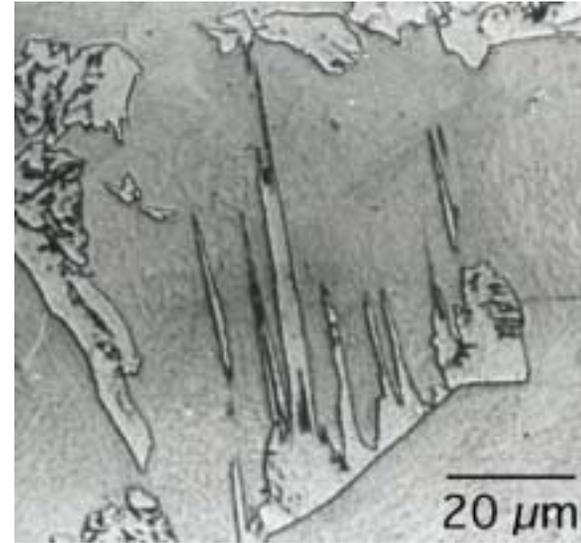
Body-centered
tetragonal
martensite

Microstructures in steels

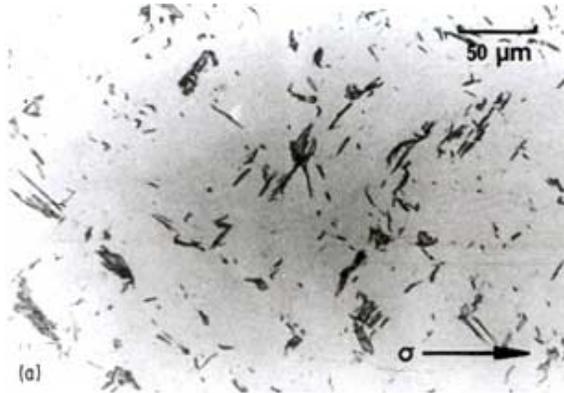


20 μm

Two-dimensional morphology of pearlite, apparently consisting of alternating layers of cementite and ferrite.

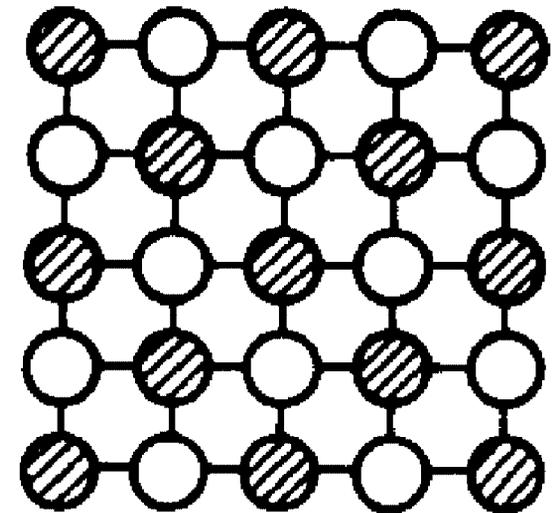
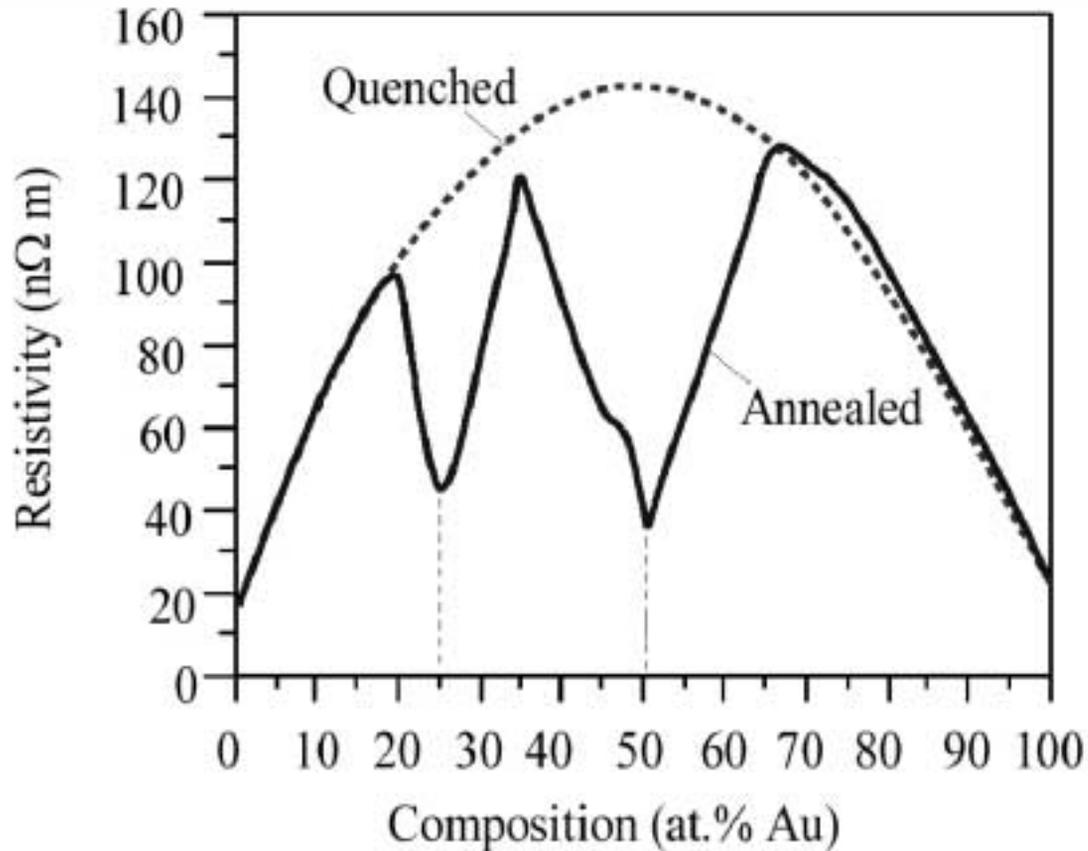


Optical micrograph of Widmanstatten ferrite in an Fe-Ni-Si-C low-alloy steel



Martensite structure.

Intermetallic compounds.



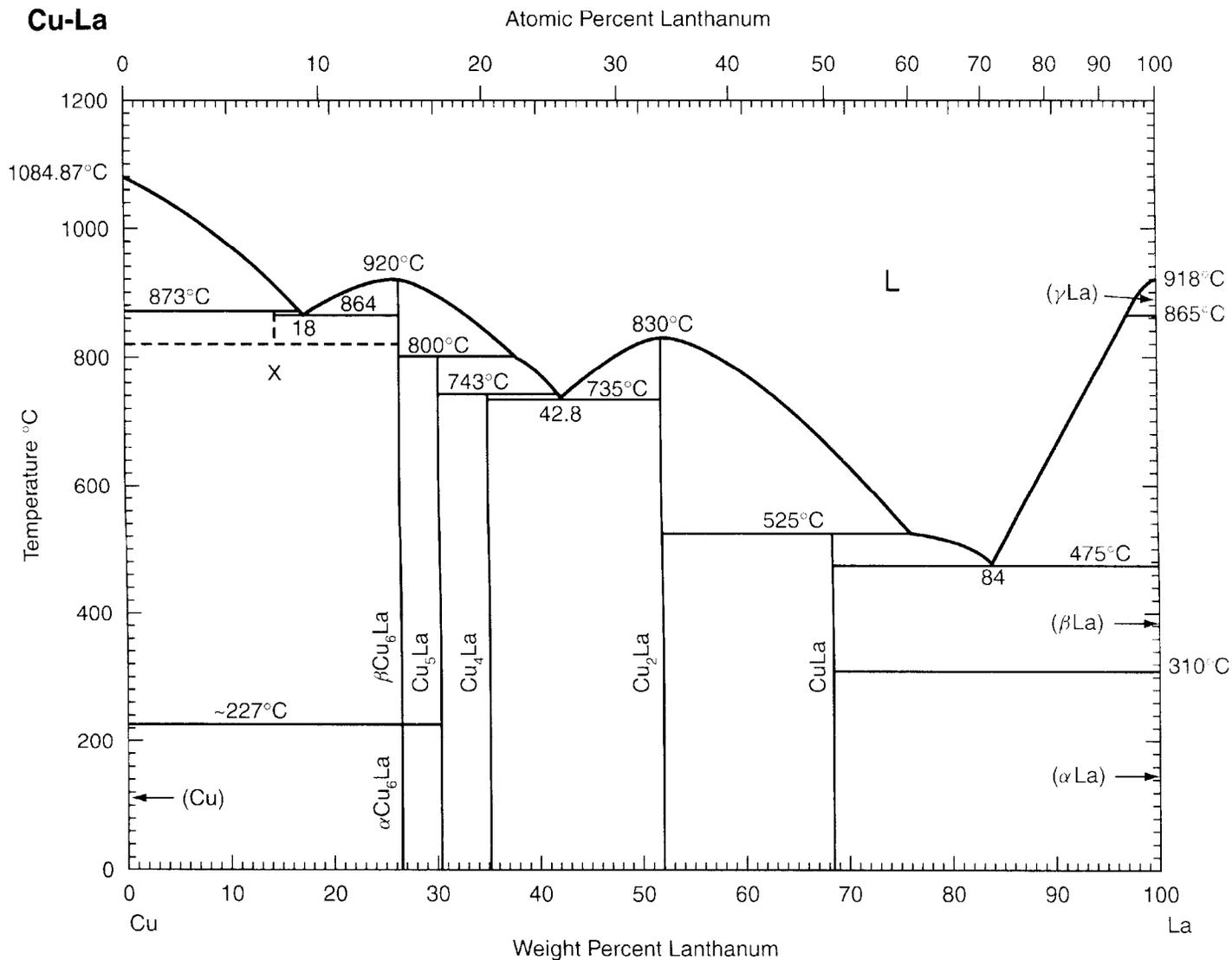
Ordered

Ordered FCC structure.

Cu-Au resistivity vs. Au content.

Ordered intermetallic compounds are formed if the components have very different electronegativity.

Cu-La intermetallic compounds.



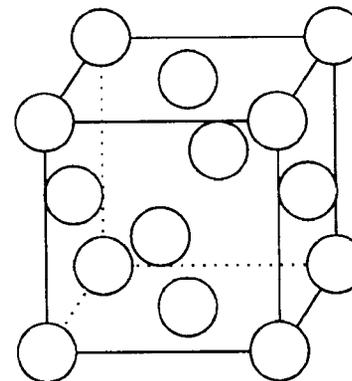
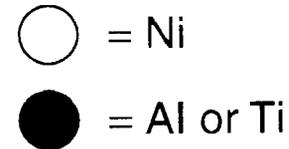
Superalloys

Superalloys is a name for a group of alloys that retain high strength at elevated temperatures.

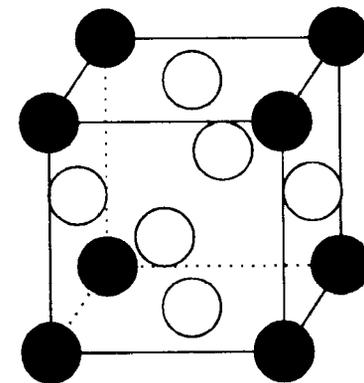
Chemical Composition (wt %) of Various Superalloys

Element	Alloy ^a							
	A	B	C	D	E	F	G	H
Al	—	—	—	1.35	—	0.2	—	—
B	—	—	—	0.005	—	—	—	—
C	0.03	0.12	0.58	0.036	—	0.05	0.1	—
Co	—	—	—	13.1	—	—	39.0	5.0
Cr	—	—	—	19.7	19.0	15.0	22.0	10.0
Fe	—	—	—	1.03	—	53.0	3.0	—
Hf	0.9	—	1.94	—	—	—	—	—
Mo	—	98.4	—	4.16	3.0	1.25	—	—
Nb	—	—	69.2	—	5.0	0.5	—	1.0
Ni	—	—	—	58.2	73.0	26.0	22.0	62.5
Si	—	—	—	0.07	—	—	—	—
Ta	89.8	—	—	—	—	—	—	12.0
Ti	1.1	1.2	—	2.95	—	2.15	—	1.5
V	—	—	—	—	—	0.2	—	—
W	8.2	—	28.3	—	—	—	14.0	4.0

The main strengthening mechanism is preventing grain boundaries from sliding via dislocation pinning (will consider it later).

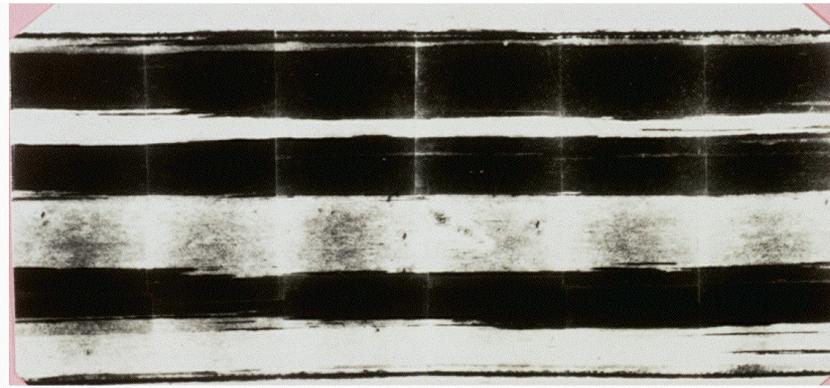
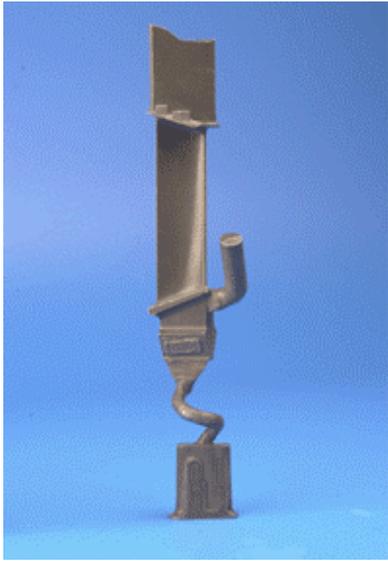


γ



γ'

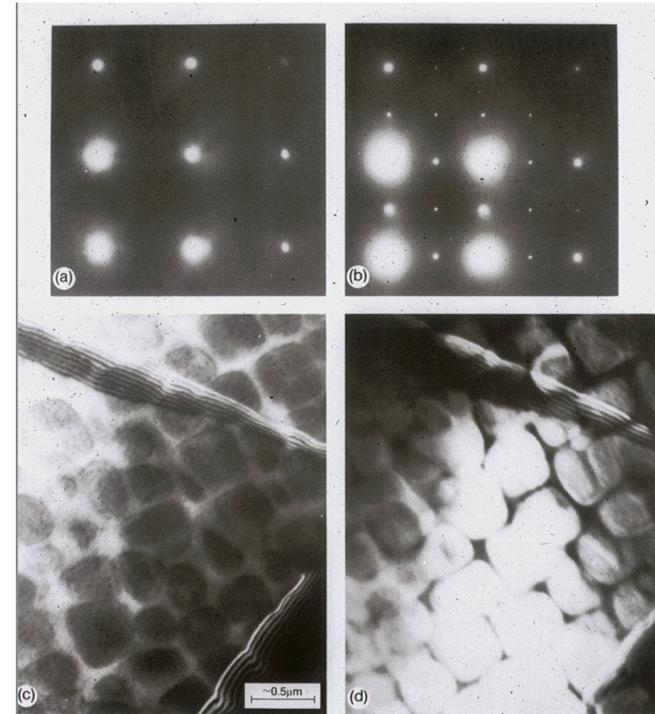
Most of the superalloys are Substitution solutions, where one of the components tends to form covalent bonds (Al in Ni_3Al , W in Ta or Nb).



200 μm

Directional recrystallization

The blade is made out of a nickel-base superalloy with a microstructure containing about 65% of gamma-prime precipitates in a single-crystal gamma matrix. The blade is directionally-solidified via a spiral selector, which permits only one crystal to grow into the blade.



Microstructure of a nickel-base superalloy

Other alloys

Alloy Designation	Detail
1XXX	99% pure aluminium
2XXX	Cu containing alloy*
3XXX	Mn containing alloy
4XXX	Si containing alloy**
5XXX	Mg containing alloy
6XXX	Mg and Si containing alloy*
7XXX	Zn containing alloy*
8XXX	Other alloys

Aluminium Beverage Can

A



Can End (5XXX Alloy – Mg rich)



Can Body (3XXX Alloy – Mn rich)



5XXX magnesium-containing

Aluminium Alloys in Aerospace



Airbus A340

Despite competition from other materials, Al alloys still make up > 70% of structure of modern commercial airliner

2XXX (Cu-containing, 500 MPa)

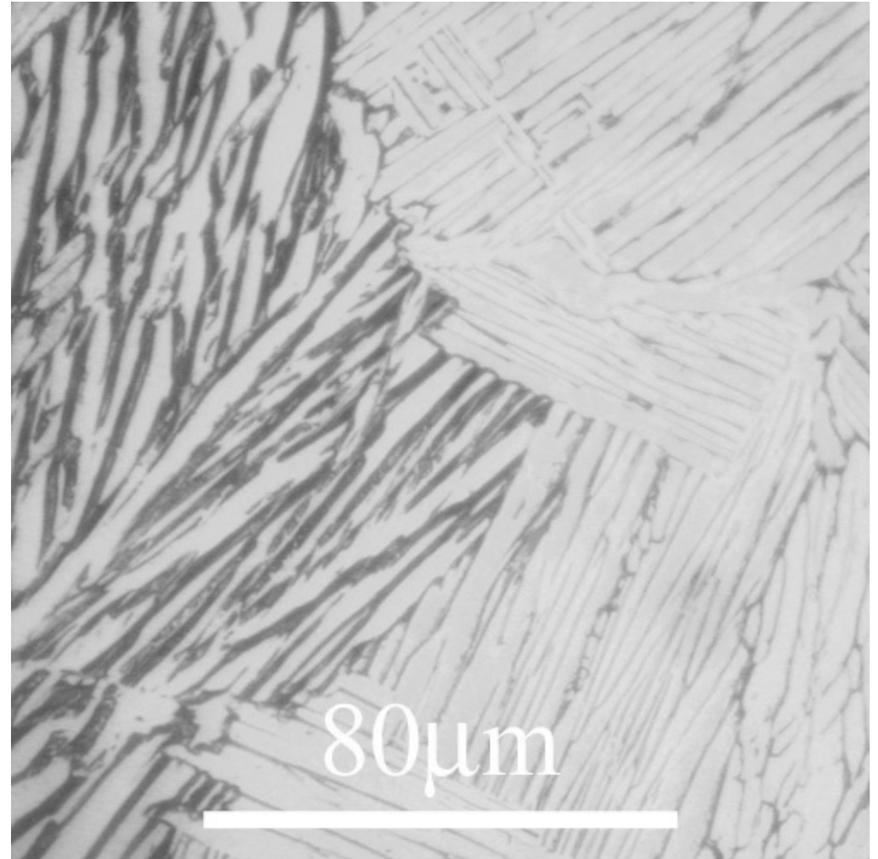
7XXX (Zn+Mg+Cu-containing, 600 Mpa)

Ti-alloys: β -titanium, BCC, stable $>890\text{ }^\circ\text{C}$.

α -titanium, HCP, stable $<890\text{ }^\circ\text{C}$.



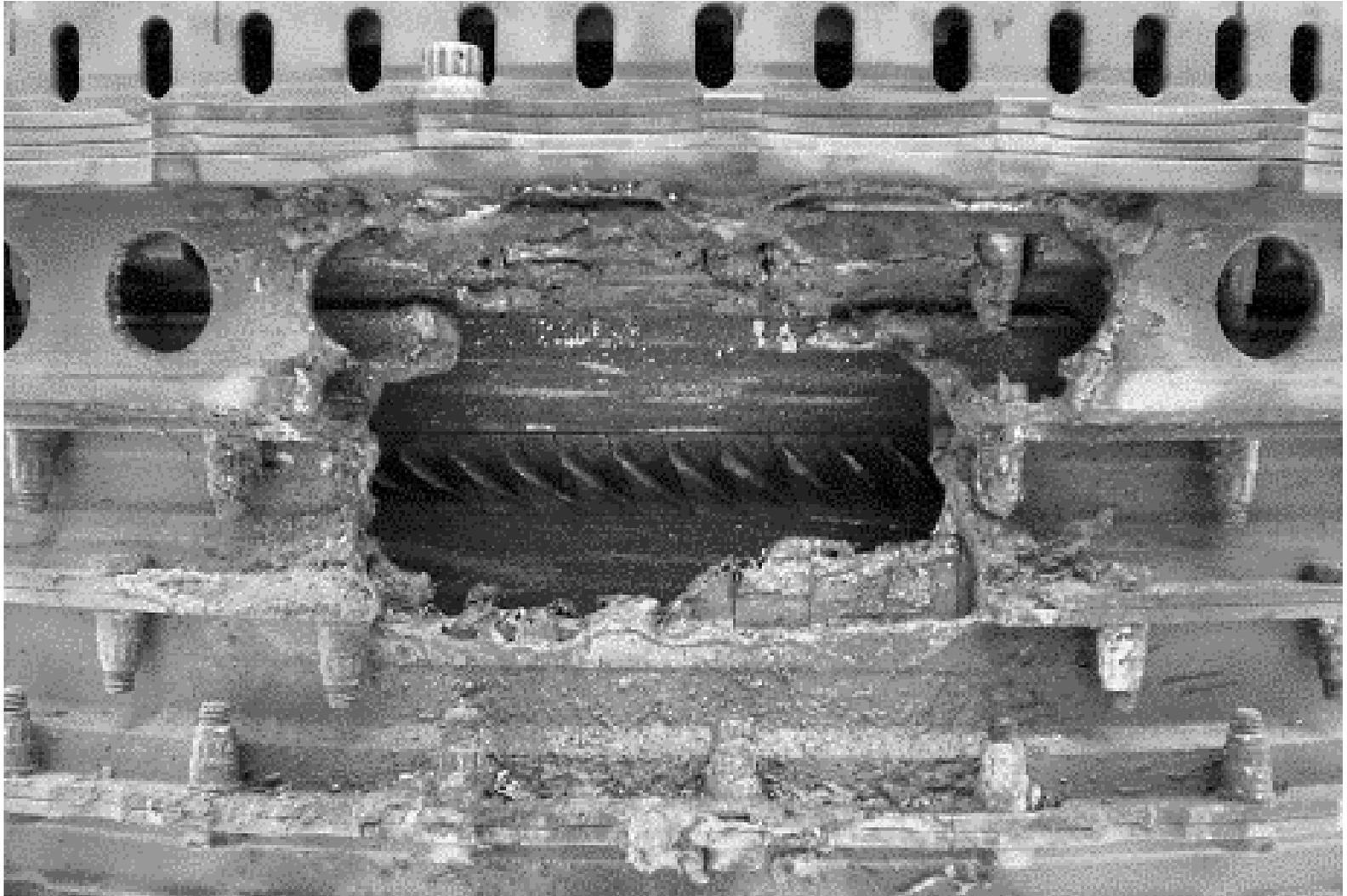
Cu-strengthened α -Ti: Ti_2Cu plates in Ti



(Al-V)-strengthened β -Ti: Ti_2Cu plates in Ti

Results of Ti-fire in jet turbine engine.

Homework: Why would you expect Ti to catch fire?



M. Hicks, Rolls-Royce