Equilibrium Phase Diagrams

A brief introduction of phase diagrams

Basic definitions

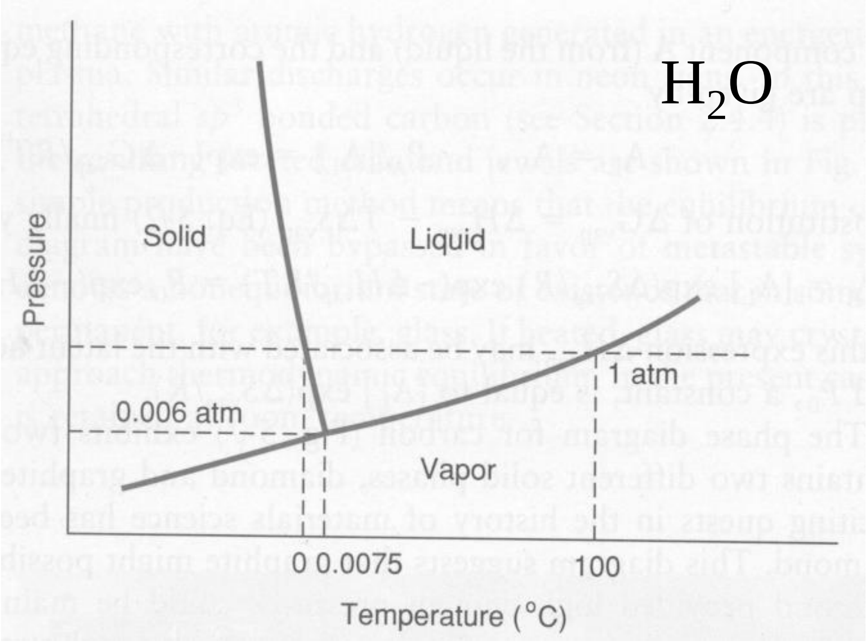
- **System**: specific body of materials under consideration, isolated from the rest of the universe for observation, has a boundary
- **Phase** : any portion of the system (including the whole of the system) that is chemically and physically homogeneous within itself, mechanically separable from the rest of system
- **Components** : smallest number of independently variable chemical constituents, necessary to describe the chemical composition of each phase in the system, e.g. Zn, Au, H_2O, Al_2O_3

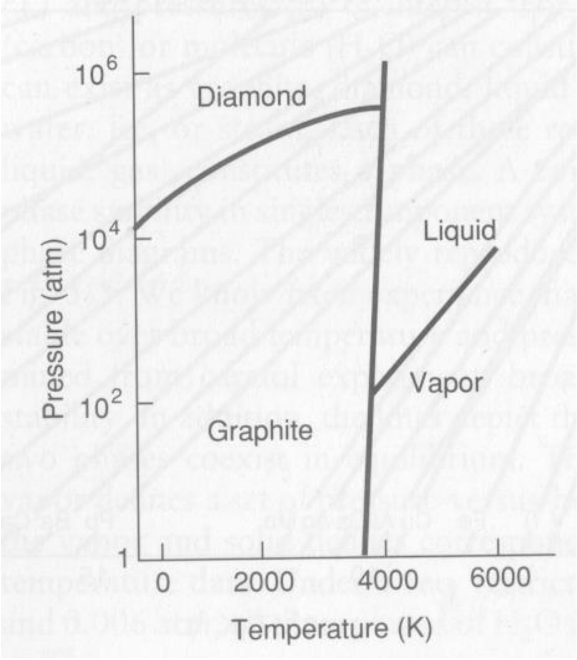
Basic definitions

- **Equilibrium**: at *equilibrium* there is a balance between opposing forces acting on the system, system is at its lowest *free energy* state, at *equilibrium* the properties of a system do not change with time, the system is stable
- **Metastable** : reaching *equilibrium* state may take a long time, then the system can exist in a *metastable* state for a very long time.
- **Phase diagram** : a graphic display of phase structure (microstructural) information. Single component phase diagrams are the simplest:

Single-component systems

- H_2O system : water-ice-vapor; phase of water
- Carbon phase diagram





- Temperature and pressure are the independent variables

GIBBS Phase Rule

$$P + F = C + 2$$

- **Degrees of Freedom, F** : number of independent variable available to the system
- P, number of Phases
- C, number of components
- Historically, temperature and pressure were the variables available to the system

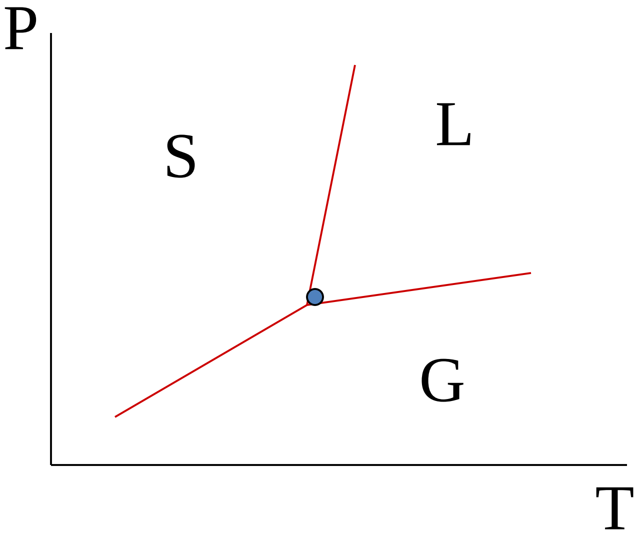
GIBBS Phase Rule

- In a single-component system

  F + P = 1 + 2 =>

  We have

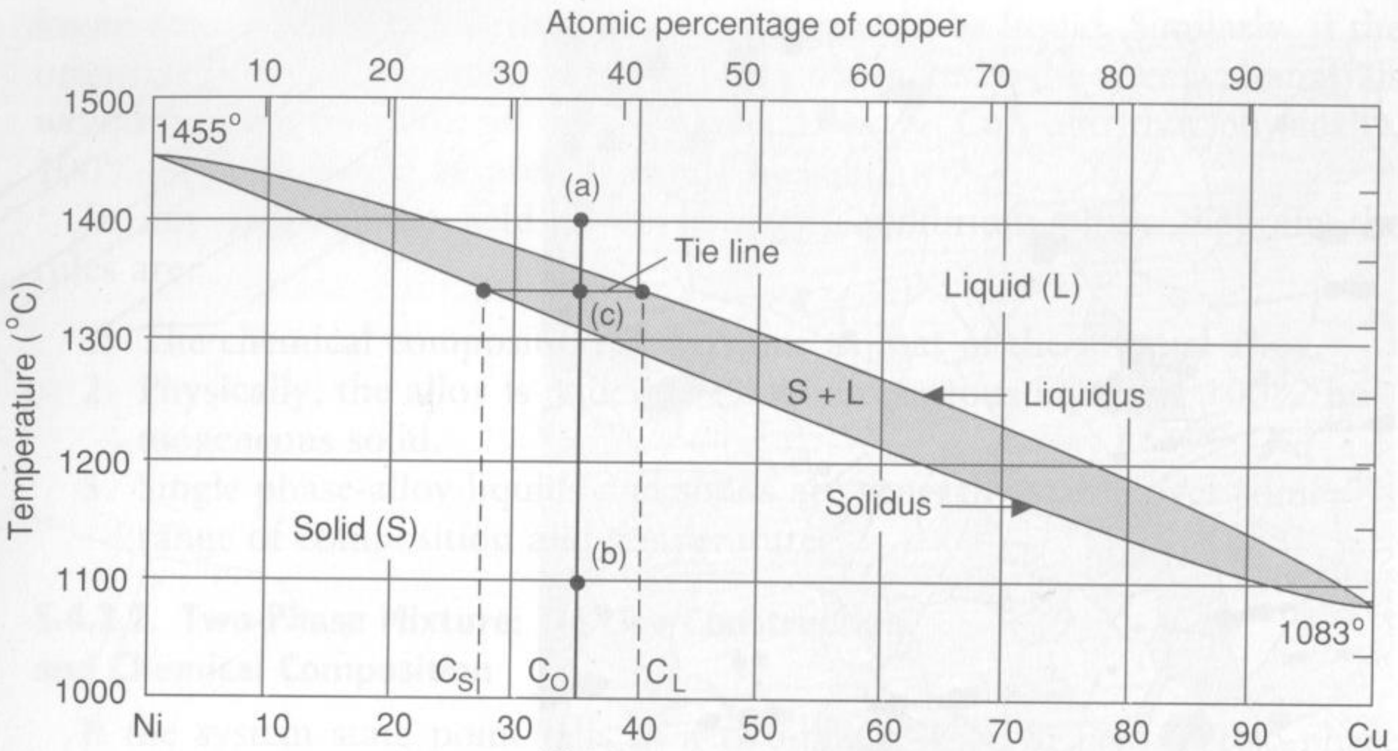
  - Di-variant fields
  - Mono-variant lines
  - Invariant point



F = number of variables you can change independently without altering the phase composition of the system

Two-components phase diagrams

- Binary phase diagrams with complete solid solubility

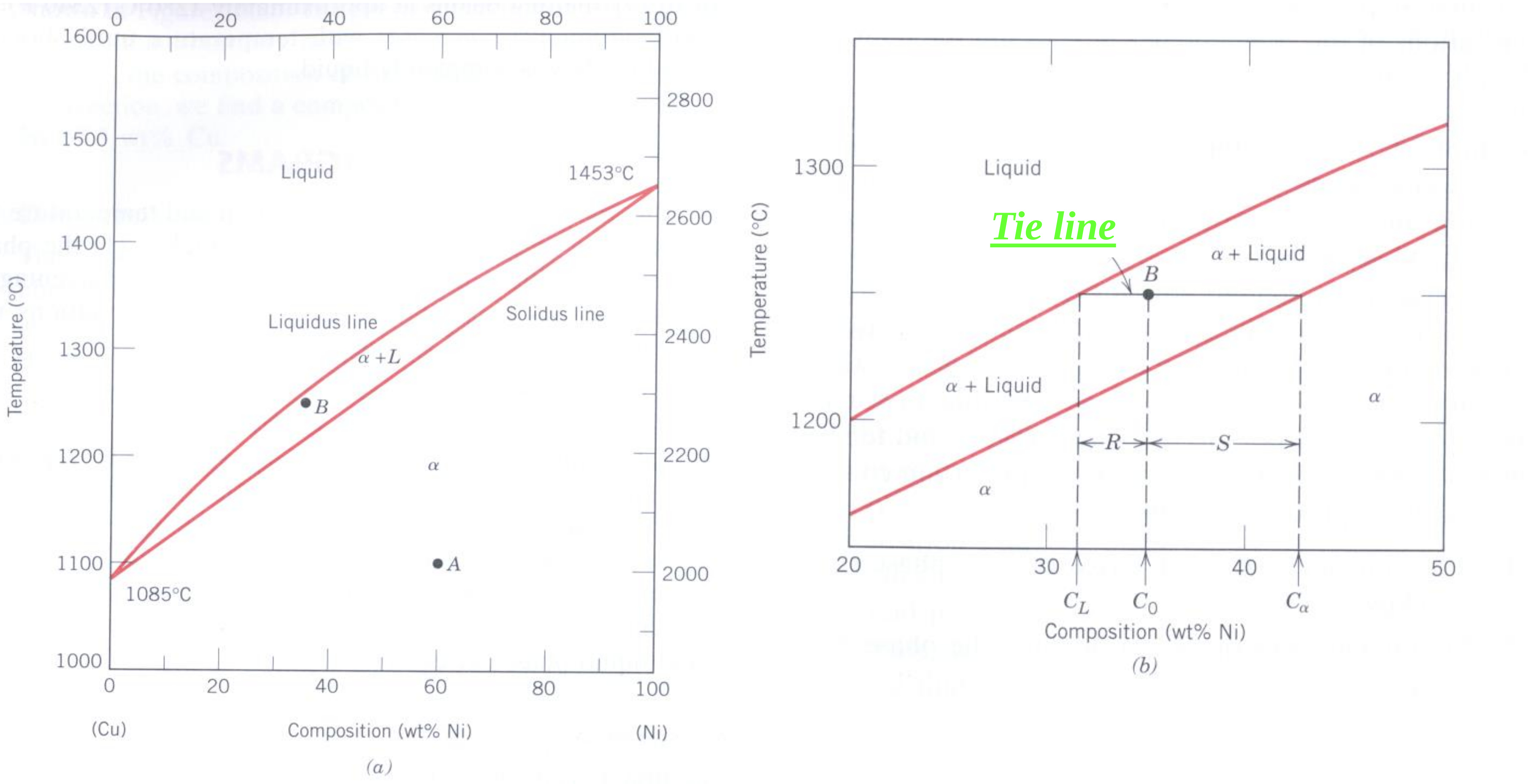


Equilibrium phase diagram of the Cu–Ni system.

- Complete substitutional solid solubility between Cu and Ni
- Cu and Ni both form FCC, have similar atomic radii, similar electro negativity and valences
- Above Liquidus Line @ all T and compositions only liquid present
- Below Solidus Line @ all T and compositions only solid phase present
- Between solidus and liquidus lines two phase region: solid phase and liquid

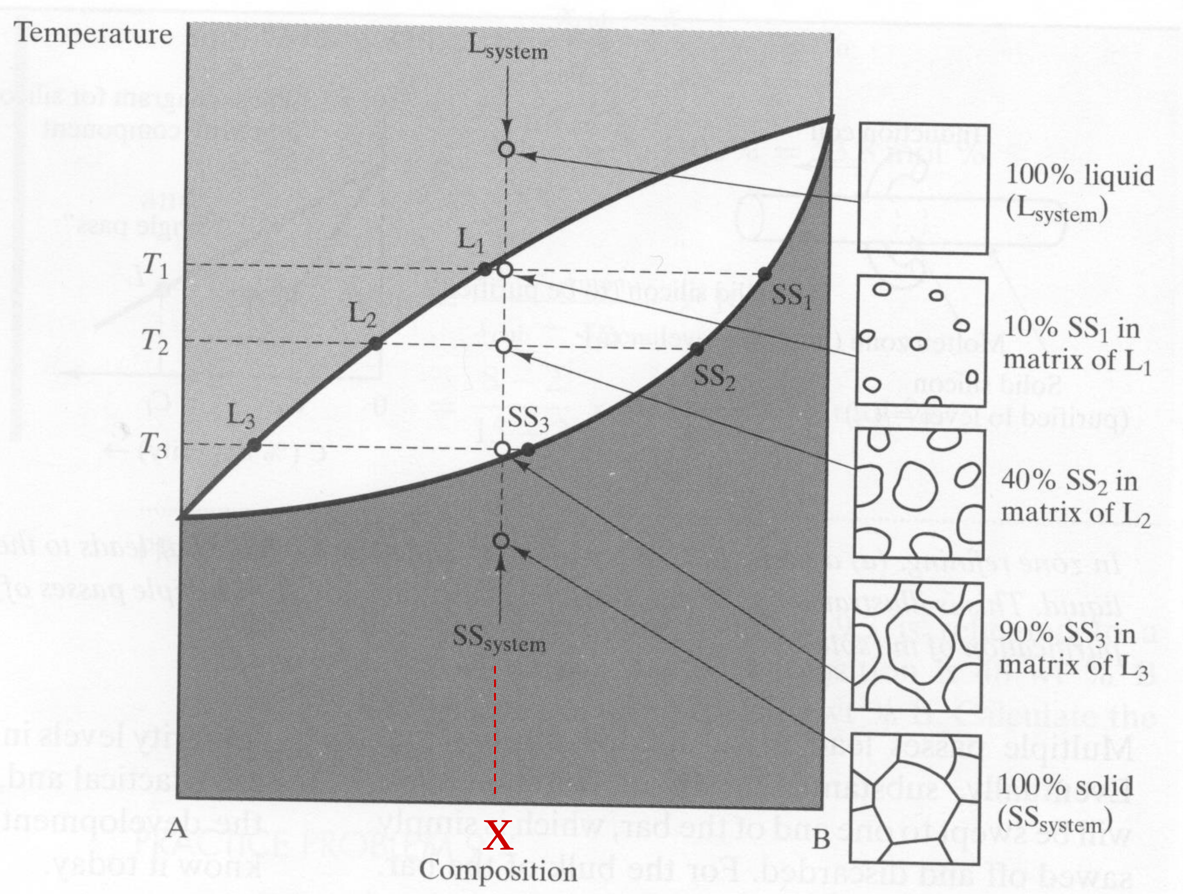
Finding the compositions of the phases in the two phase region:

Tie-Line construction



Development of the microstructure: (complete solubility)

Under equilibrium conditions



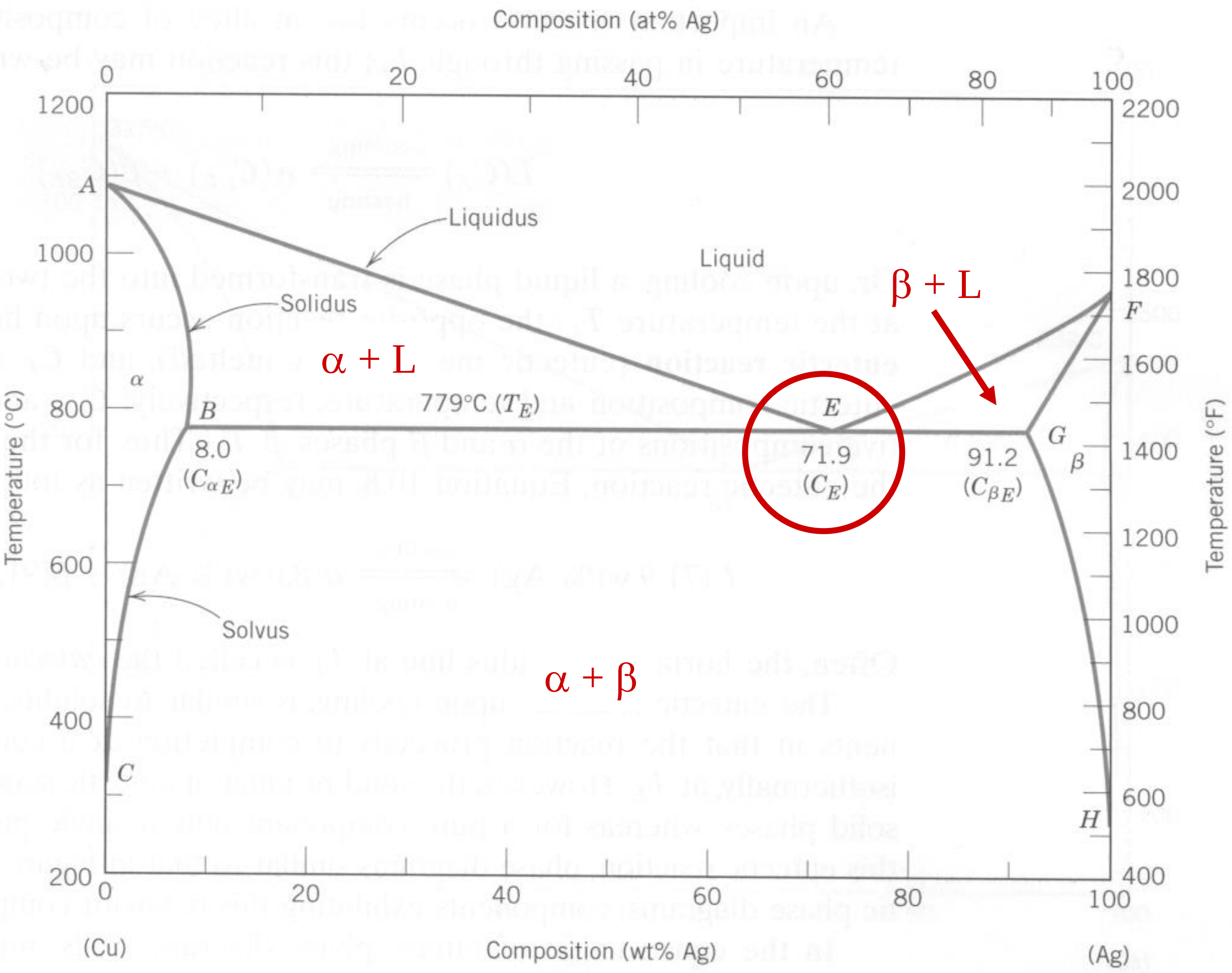
igure 9.33 *Microstructural development during the slow cooling of a 50% A–50% B composition in a phase diagram with complete solid solution. At each temperature, the amounts of the phases in the microstructure correspond to a lever-rule calculation. The microstructure at T_2 corresponds to the calculation in Figure 9.31.*

As a homogeneous liquid with the composition x cools, the contents of a crucible goes through structural changes as one crosses phase boundary lines.

In two phase regions, tie line indicates the compositions of the phases, and the lever rule can be used to find the amounts of phases in the crucible.

At the end of the equilibrium (slow) cooling crucible will contain a homogeneous solid Solution of composition x.

Binary Eutectic Systems: limited solubility (Under equilibrium conditions)



- •Three two-phase regions
- •Two solid solutions with limited solubility
- •A Composition that melts at a lower temperature (Eutectic temp.) than both pure phases, eutectic point, E

Binary Eutectic Systems: limited solubility (Under equilibrium conditions)

@ Eutectic point:

$L_E \rightarrow \alpha_E + \beta_E$ @ eutectic temperature T_E

- In a eutectic binary phase diagram, three phases can be in equilibrium, at points along the eutectic isotherm.
- Single phase regions are always separated from each other by a two phase region consisting of two single phases that border the two phase region
- The eutectic point, E is the invariant point in the system

Development of the microstructure: Eutectic system

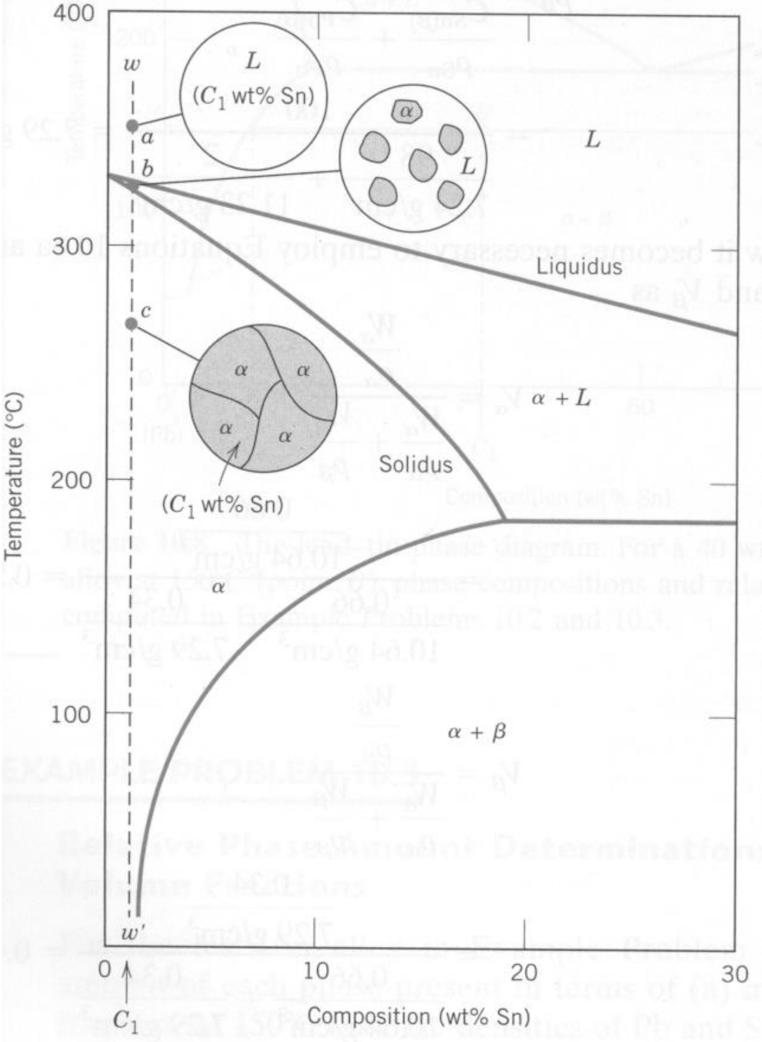


Figure 10.9 Schematic representations of the equilibrium microstructures for a lead–tin alloy of composition C_1 as it is cooled from the liquid-phase region.

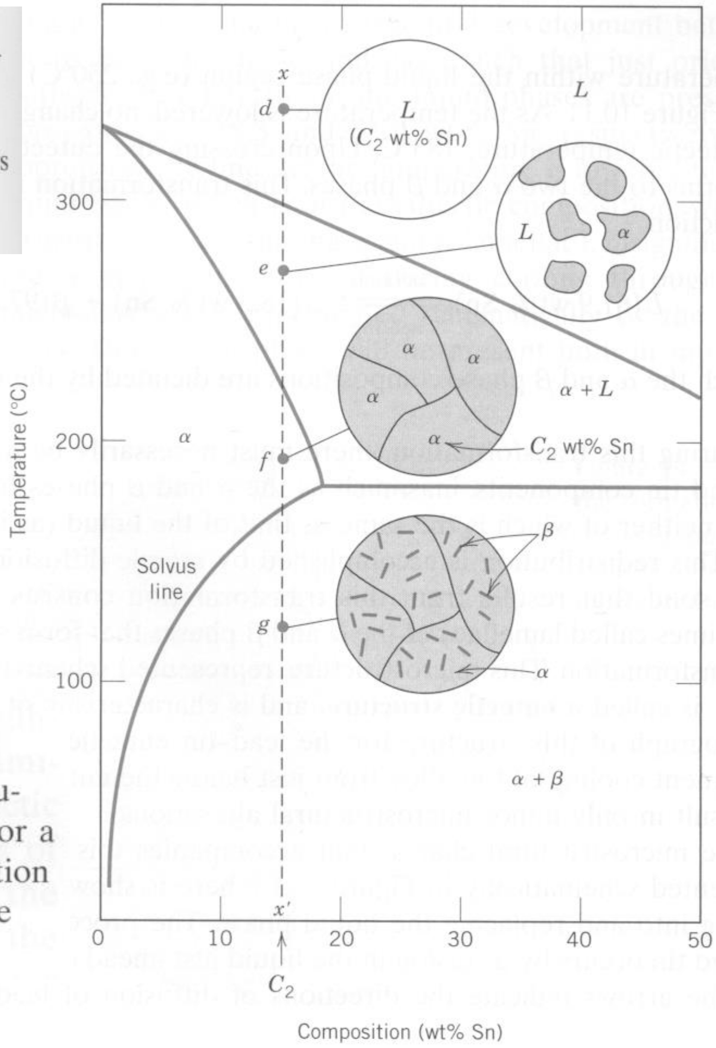
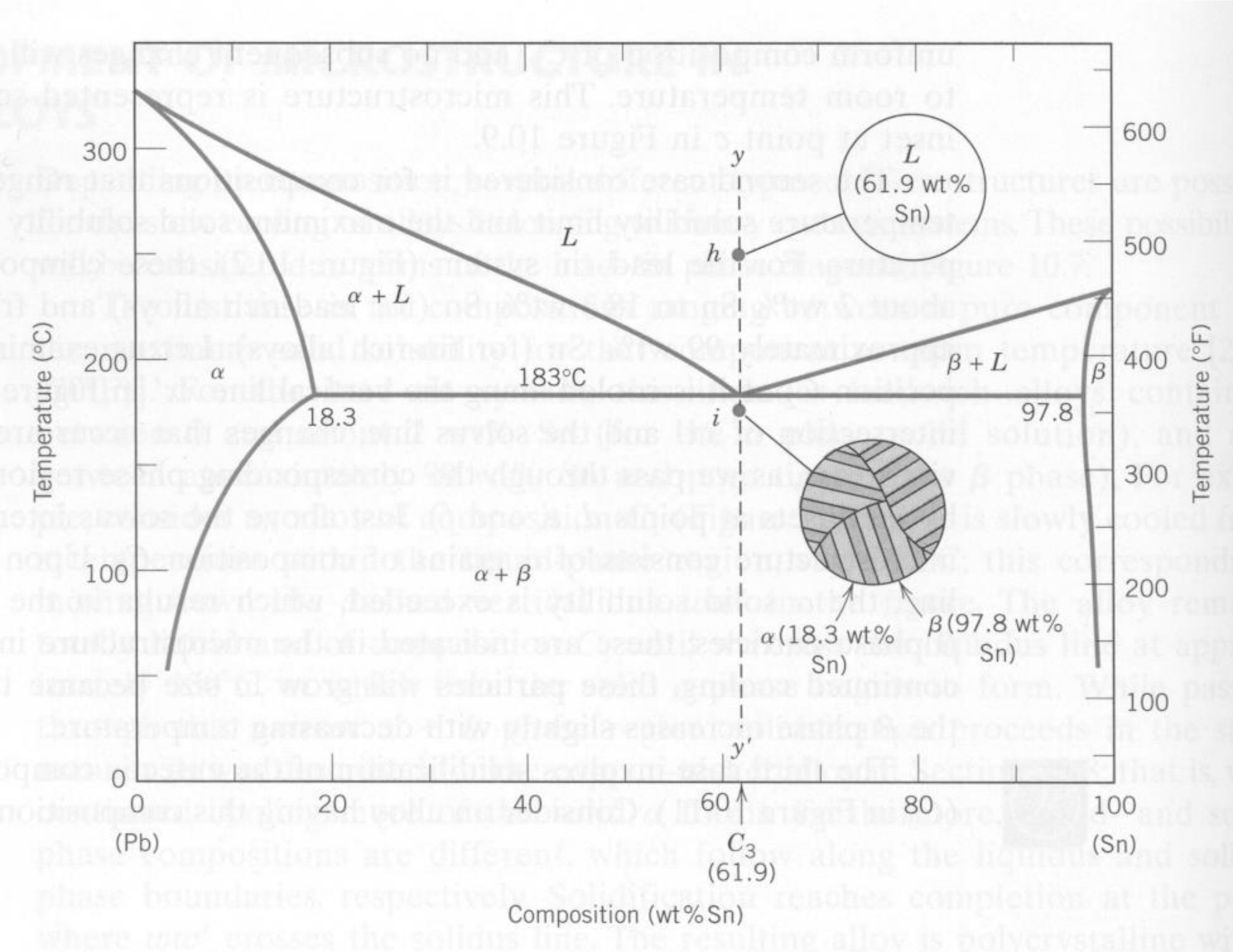


Figure 10.10 Schematic representations of the equilibrium microstructures for a lead–tin alloy of composition C_2 as it is cooled from the liquid-phase region.

Development of the microstructure: Eutectic system

eutectic reaction and eutectic microstructure



Development of the microstructure: Eutectic system

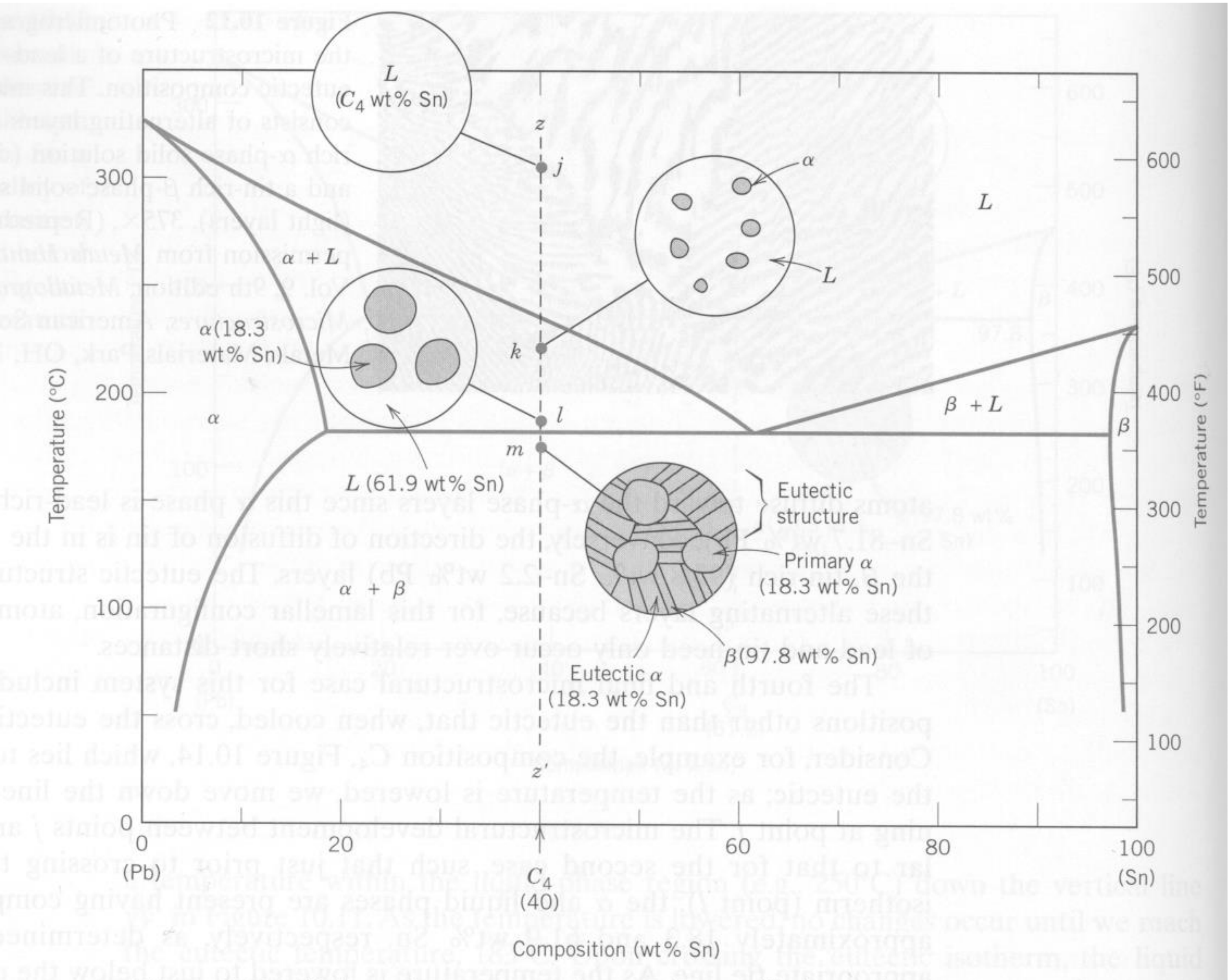


Figure 10.14 Schematic representations of the equilibrium microstructures for a lead–tin alloy of composition C_4 as it is cooled from the liquid-phase region.

Binary phase diagrams with intermediate compounds

Simplest case a congruently melting binary compound

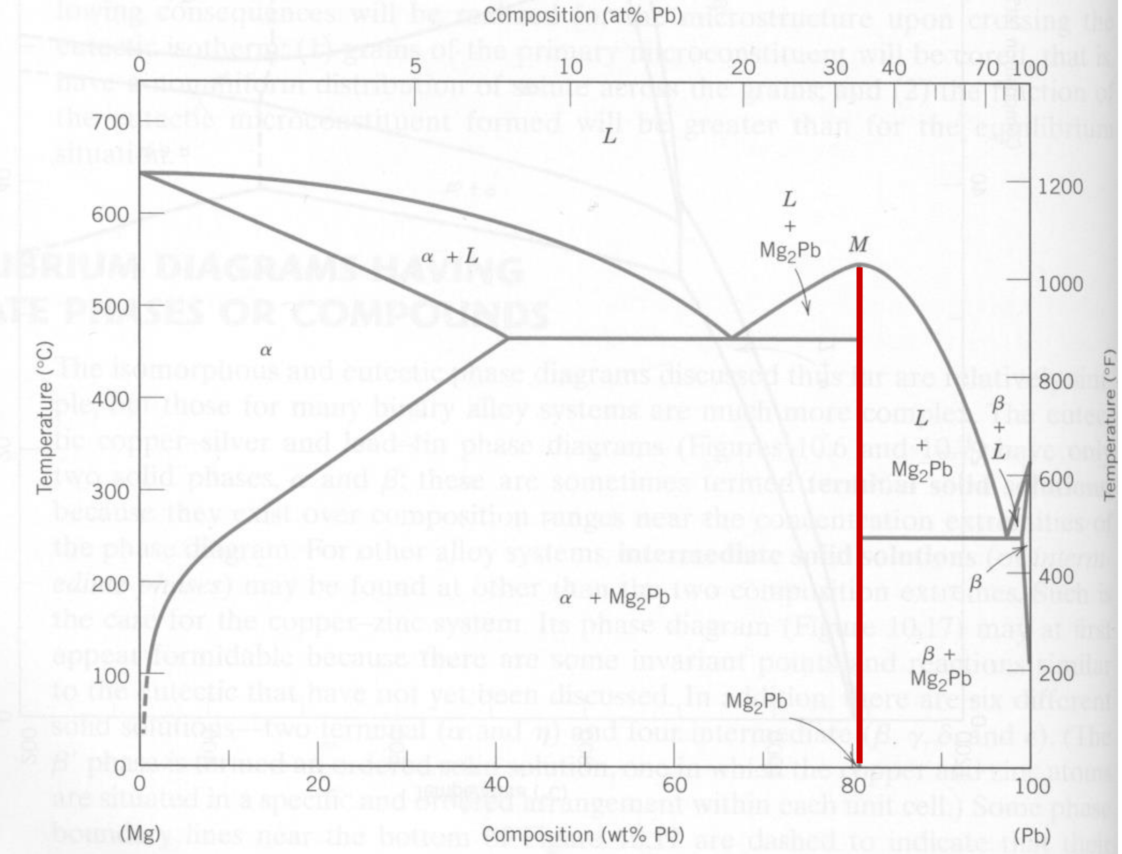


Figure 10.18 The magnesium–lead phase diagram. (Adapted from *Phase Diagrams of Binary Magnesium Alloys*, A. A. Nayeb-Hashemi and J. B. Clark, Editors, 1988. Reprinted by permission of ASM International, Materials Park, OH.)

- A congruently melting compound divides a simple eutectic into two simple eutectics.
- The compounds melts directly into a liquid with the same composition

In real life they may look more like this or a bit colorful (-:

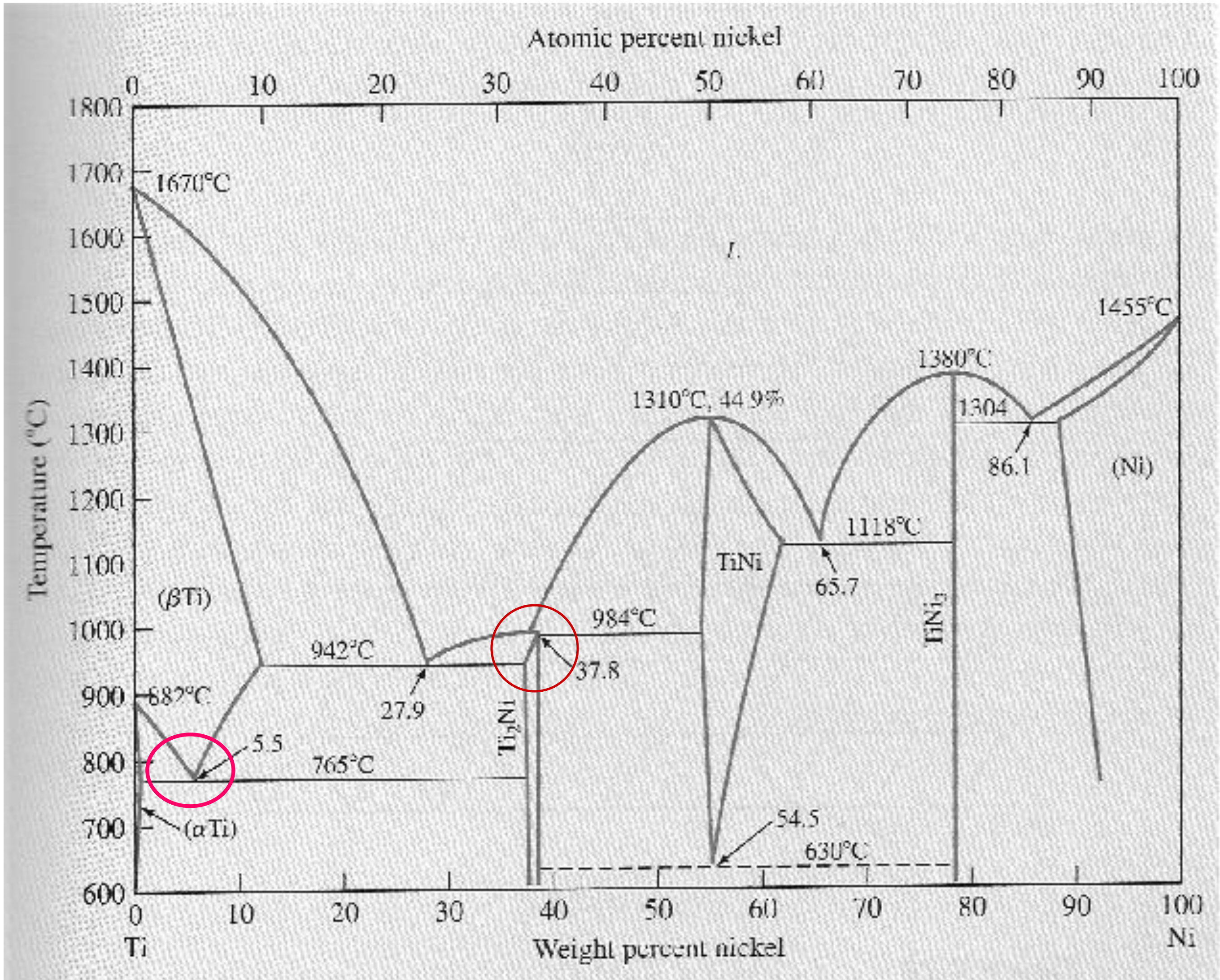


Figure EP8.8
Titanium-nickel phase diagram.
(After Binary Alloy Phase Diagrams, ASM Int., 1986, p. 1768.)

Even this one is not too bad. There are two new types of reactions: Eutectoid and Peritectic reactions; besides there are intermediate compounds that have solubilities on both sides; e.g. TiNi

Eutectoid and Peritectic reactions:

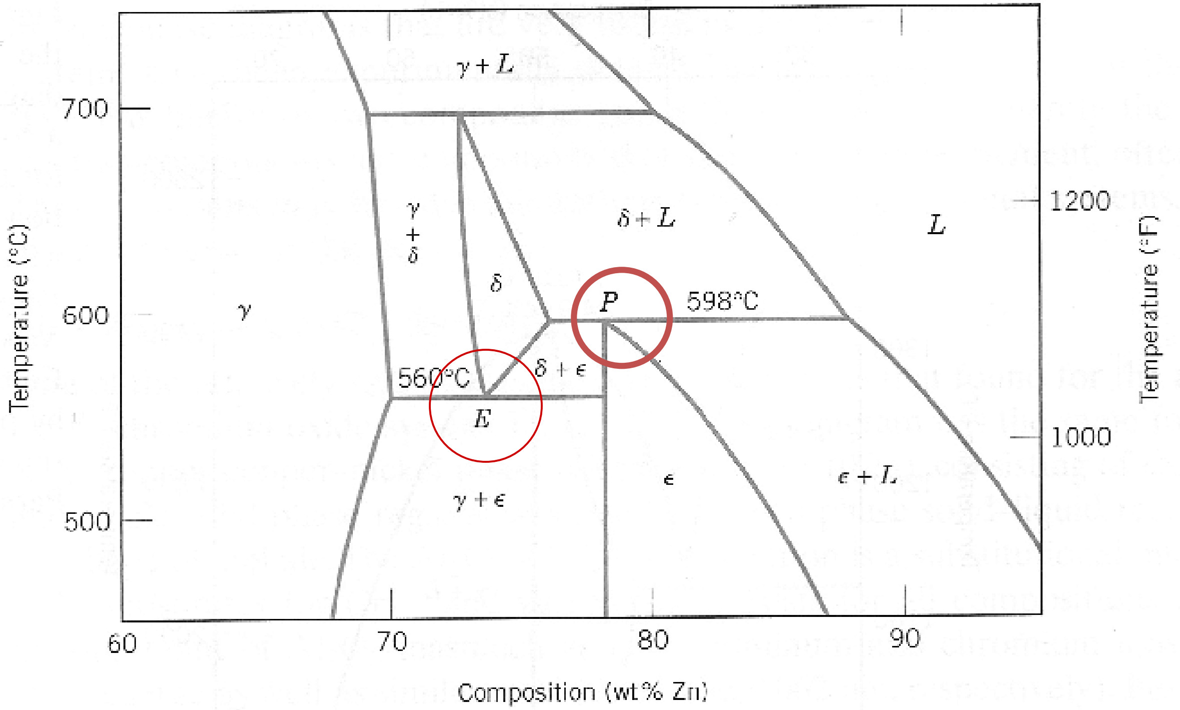


Figure 10.19 A region of the copper–zinc phase diagram that has been enlarged to show eutectoid and peritectic invariant points, labeled *E* (560°C, 74 wt% Zn) and *P* (598°C, 78.6 wt% Zn), respectively. (Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 2, T. B. Massalski, Editor-in-Chief, 1990. Reprinted by permission of ASM International, Materials Park, OH.)

Eutectoid rxn

δ ←→ γ + ∈

Peritectic rxn

δ + L ←→ ∈

MME-2506 Refractory Materials

Refractories are heat resistant materials used in almost all processes involving high temperatures and/or corrosive environment. These are typically used to insulate and protect industrial furnaces and vessels due to their excellent resistance to heat, chemical attack and mechanical damage.

Heat resistant, heat insulation, high T, resistance to chemical attack, resistant to mechanical damage (compressive) → **Ceramics**

Ceramics are in the form of minerals in nature. They are mined and beneficiated. There are also ceramics that has to be synthesized. Since ceramic production starts from powders, final properties of ceramics are affected strongly by powder properties.

First look at raw materials as ceramic source.

Raw Materials

From the earth's crust → minerals containing Mg,Fe,Al,Ca,SiO_2 mined and beneficiated

Physical beneficiation → crushing, grinding
Chemical beneficiation → dissolution in a proper solvent and filtration

Silica

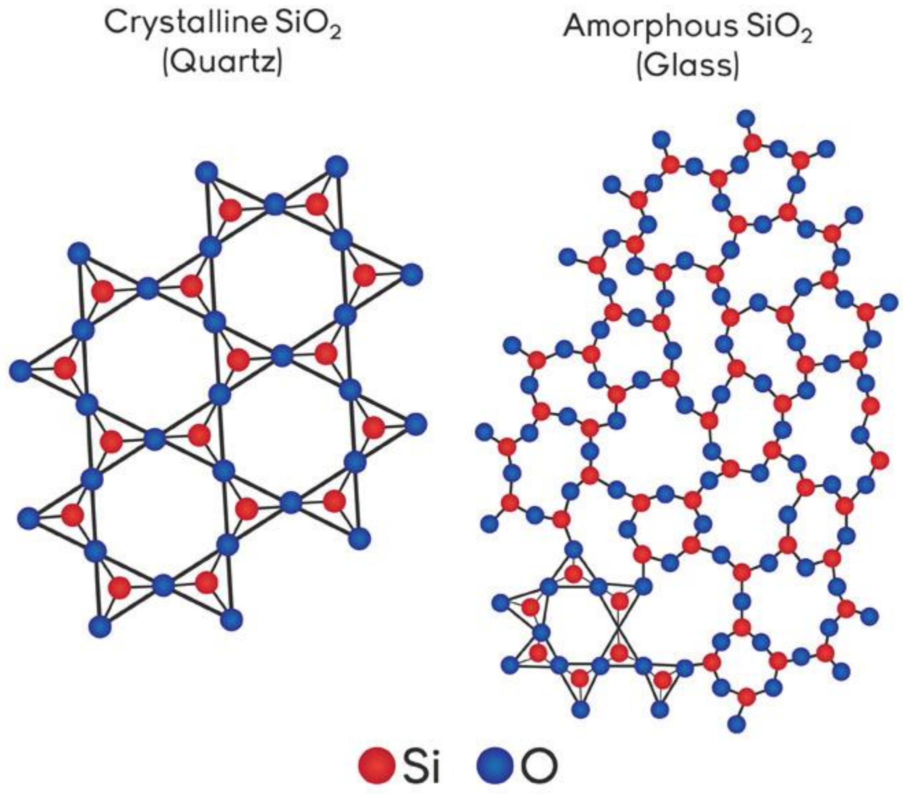
Silica is an important raw material for ceramis. Mainly used in cement and glass industry.
There are also lots of production method and application area of Silica, such as;

- Fumed Silica (colloidal silica from $SiCl_4$)
- Silica Fume (nanosized and amorphous silica as by product of Si and ferrosilicon alloys)
- Silica in microelectronics (thermal oxidation on Si layers)
- Silica Gel (acidification of sodium silicate)

Silica

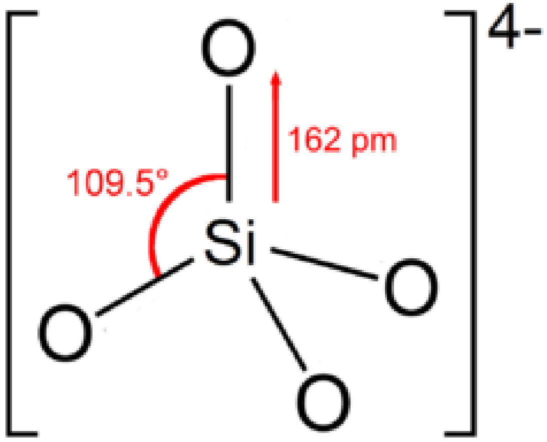
Major Silica source for glass industry is silica sand, quartz.

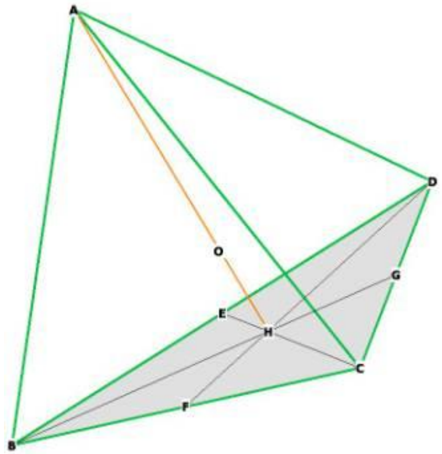
Quartz is the general name of the crystal SiO_2 , and also RT crystal structure name of SiO_2. (The other polymorph names are tridymite and cristobalite)



Silicates

Silicates that we will examine are Feldspar, kaolin, mica and mullite. They all have tetrahedrons of Si at the center and oxygens at the corners.

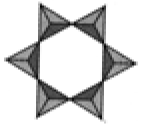
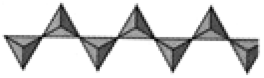
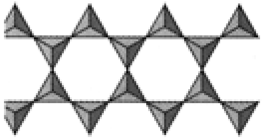
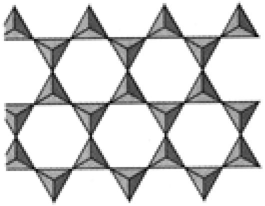
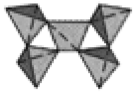




These tetrahedra sometimes occur as isolated SiO_4^{4-} centres, but most commonly, the tetrahedra are joined together in various ways, such as pairs ($Si_2O_7^{6-}$) and rings ($Si_6O_{18}^{12-}$). Commonly the silicate anions are chains, double chains, sheets, and three-dimensional frameworks.

TABLE 2.2

Major Silicate Structures

GEOMETRY OF LINKAGE OF SiO_4 TETRAHEDRA		EXAMPLE MINERAL	CHEMICAL COMPOSITION
Isolated tetrahedra: No sharing of oxygens between tetrahedra; individual tetrahedra linked to each other by bonding to cation between them		Olivine	Magnesium-iron silicate
Rings of tetrahedra: Joined by shared oxygens in three-, four-, or six-membered rings		Cordierite	Magnesium-iron-aluminum silicate
Single chains: Each tetrahedron linked to two others by shared oxygens; chains bonded by cations		Pyroxene	Magnesium-iron silicate
Double chains: Two parallel chains joined by shared oxygens between every other pair of tetrahedra; the other pairs of tetrahedra bond to cations that lie between the chains		Amphibole	Calcium-magnesium-iron silicate
Sheets: Each tetrahedron linked to three others by shared oxygens; sheets bonded by cations		Kaolinite Mica (muscovite)	Aluminum silicate Potassium-aluminum silicate
Frameworks: Each tetrahedron shares all its oxygens with other SiO_4 tetrahedra (in quartz) or AlO_4 tetrahedra		Feldspar (orthoclase) Quartz	Potassium-aluminum silicate Silicon dioxide

Feldspar

Aluminium silicate of potassium, sodium, calcium, and/or lithium. Feldspars are important ingredients in clay bodies and glazes. In both applications, their primary function is to supply fluxes to the formulations, but they also provide additional alumina (Al_2O_3) and silica (SiO_2).

Feldspars are naturally occurring minerals and are generally classified as either potash (potassium) or soda (sodium) feldspars based upon the predominant alkali metal element (the flux) that is present. Present in volcanic and metamorphic rocks.

Potash feldspars $K_2O{\bullet}Al_2O_3{\bullet}6SiO_2$

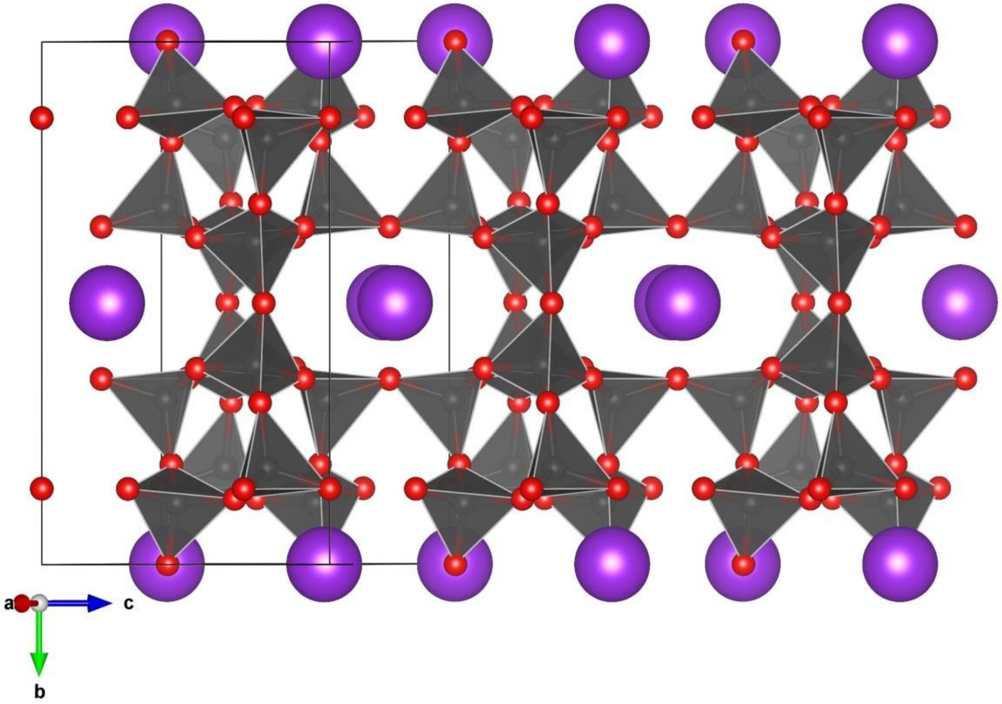
Soda feldspars $Na_2O{\bullet}Al_2O_3{\bullet}6SiO_2$

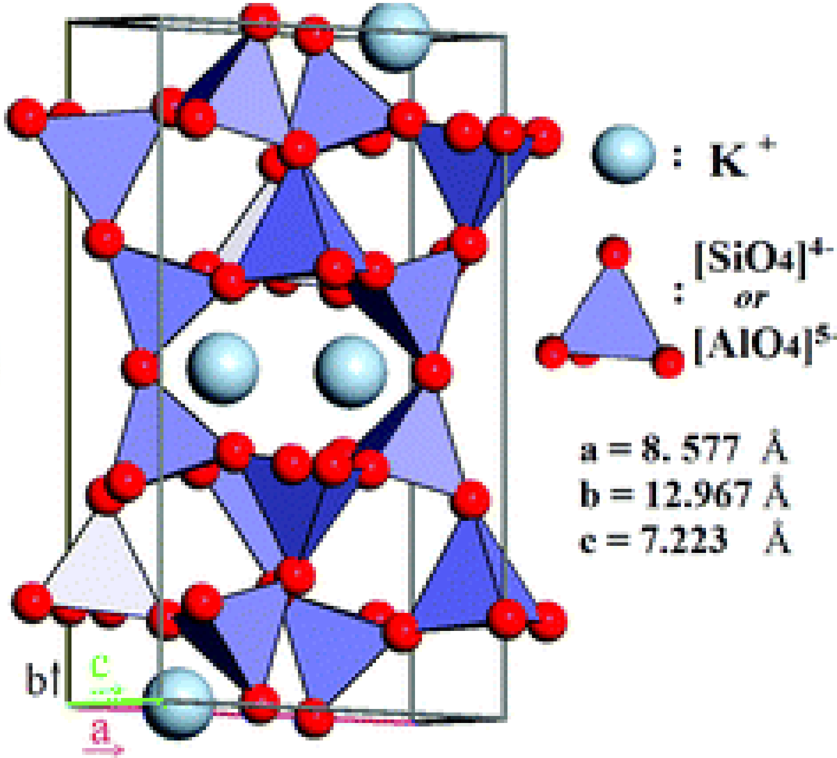
A **ceramic flux** functions by promoting partial liquification in clay bodies and glazes. Fluxes are used in glazes to lower the high melting point of the glass formers like silica

Feldspar

Potash feldspars $K_2O \bullet Al_2O_3 \bullet 6SiO_2$

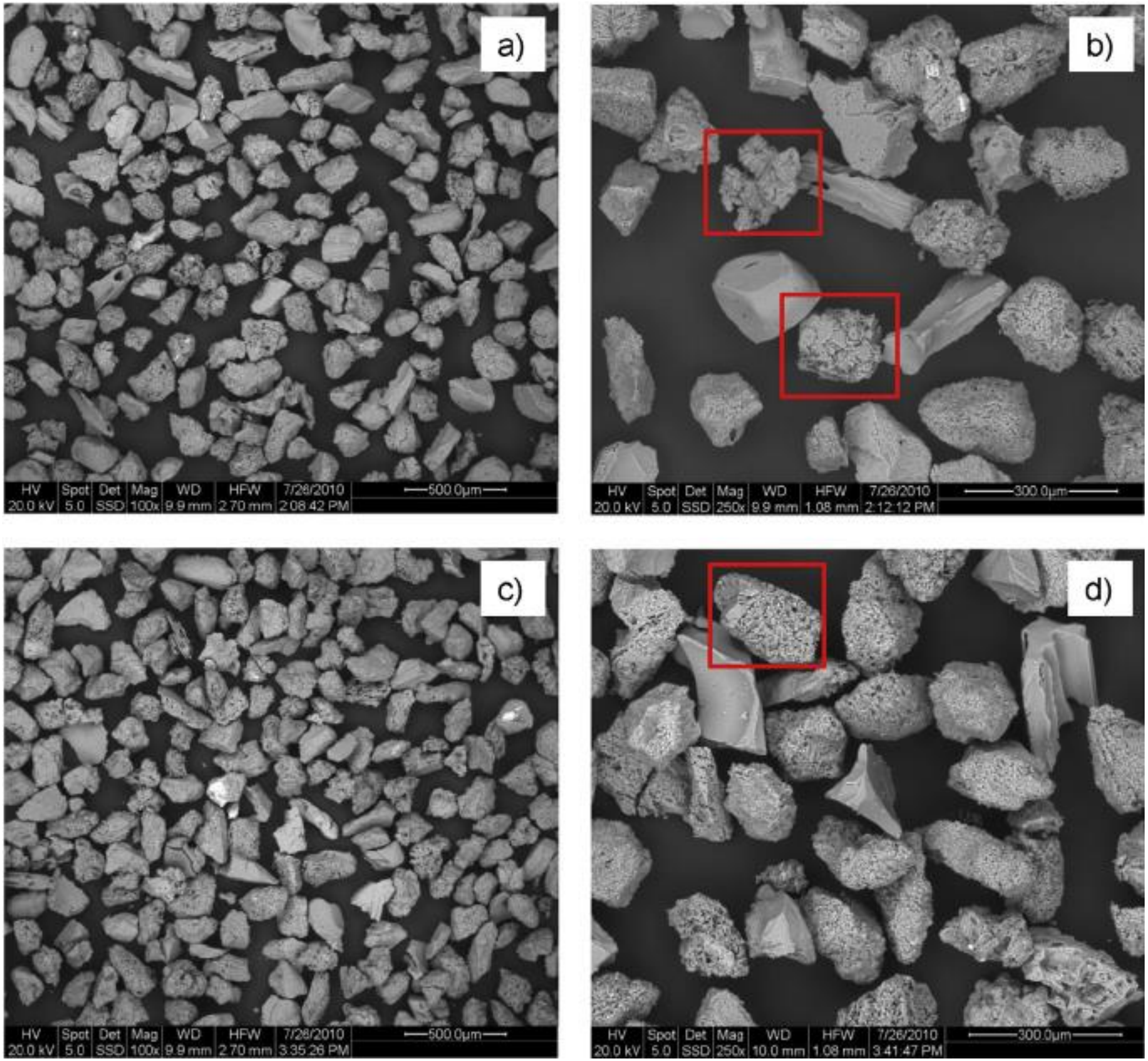
Soda feldspars $Na_2O \bullet Al_2O_3 \bullet 6SiO_2$





a = 8. 577 Å
b = 12.967 Å
c = 7.223 Å

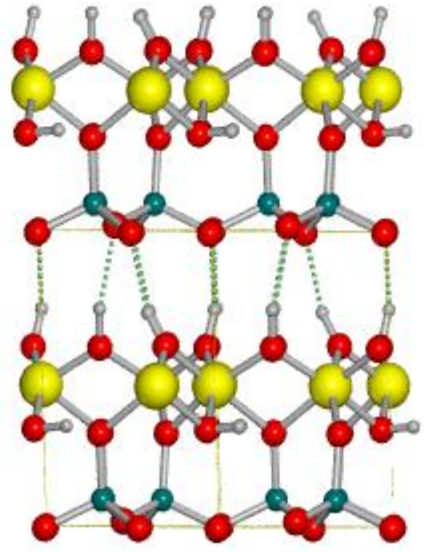
Feldspar

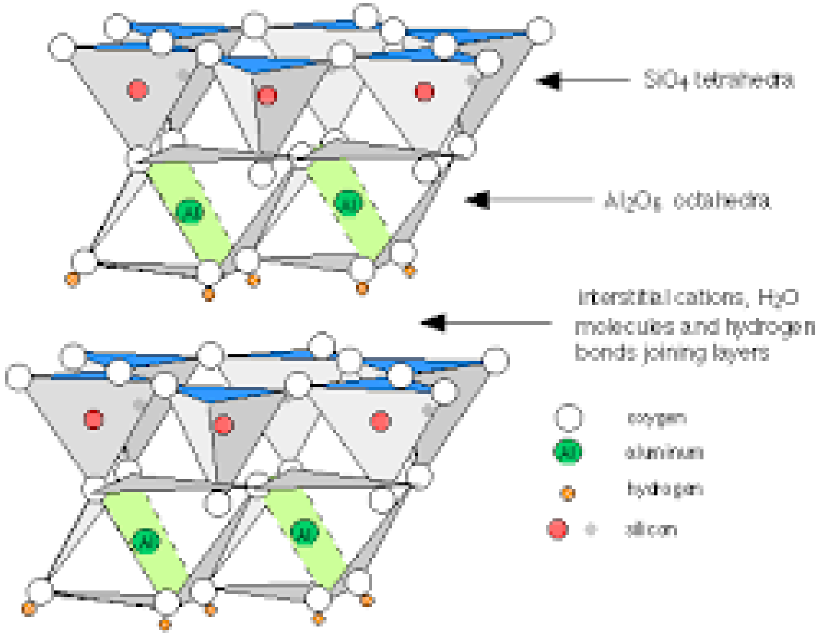

a)
HV 20.0 kV | Spot 5.0 | Det SSD | Mag 100x | WD 9.9 mm | HFW 2.70 mm | 7/26/2010 2:08:42 PM
500.0μm
b)
HV 20.0 kV | Spot 5.0 | Det SSD | Mag 250x | WD 9.9 mm | HFW 1.08 mm | 7/26/2010 2:12:12 PM
300.0μm
c)
HV 20.0 kV | Spot 5.0 | Det SSD | Mag 100x | WD 9.9 mm | HFW 2.70 mm | 7/26/2010 3:35:26 PM
500.0μm
d)
HV 20.0 kV | Spot 5.0 | Det SSD | Mag 250x | WD 10.0 mm | HFW 1.08 mm | 7/26/2010 3:41:47 PM
300.0μm

Kaolin

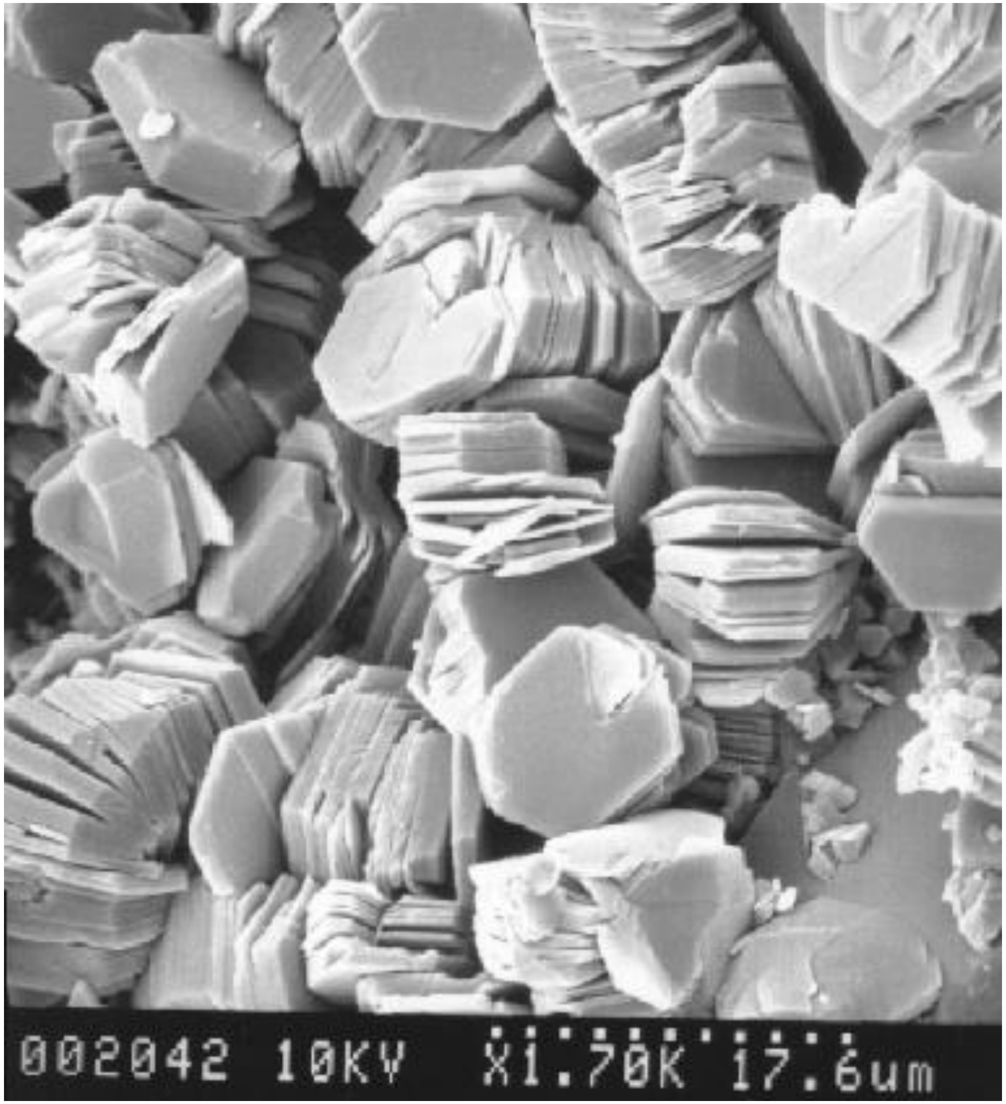
Kaolin is a clay mineral. Clay minerals are layered silicates. Rocks that are rich in kaolinite are called as Kaolin or China Clay

Kaolinite : $Al_2Si_2O_5(OH)_4$ (Si_2O_5 and $Al_2(OH)_4$)





Kaolin



hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 * *	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	ununnilium 110 **Uun** [271]	unununium 111 **Uuu** [272]	ununbium 112 **Uub** [277]		ununquadium 114 **Uuq** [289]				

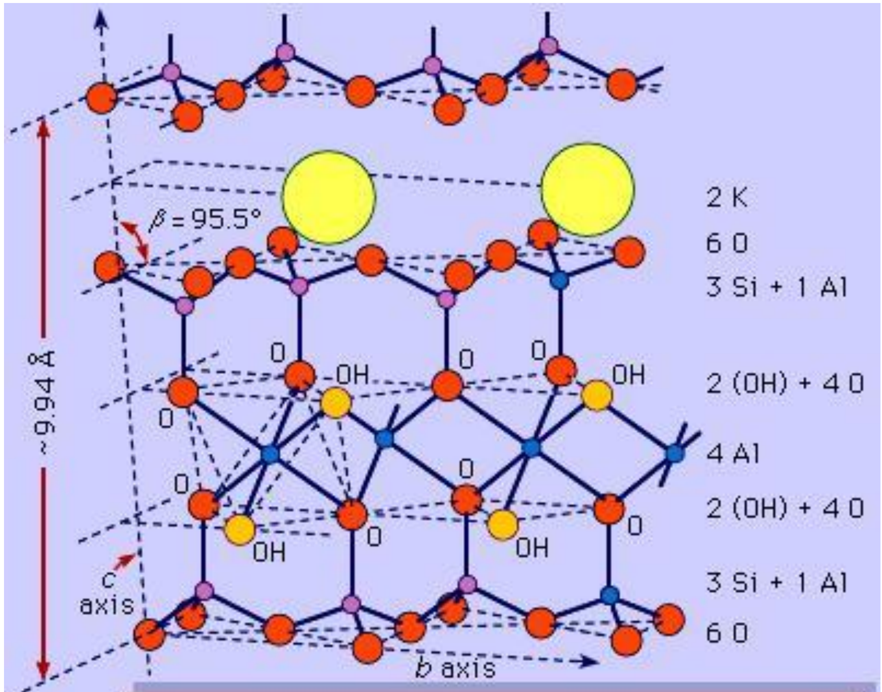
*Lanthanide series	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.04
* *Actinide series	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

Mica

There are 2 classes of mica. True and Brittle.
True micas contain univalent cations (Na^+ or K^+) btw each pair of layes. These layers are sparated under shear stress in cleavage/splitting manner.

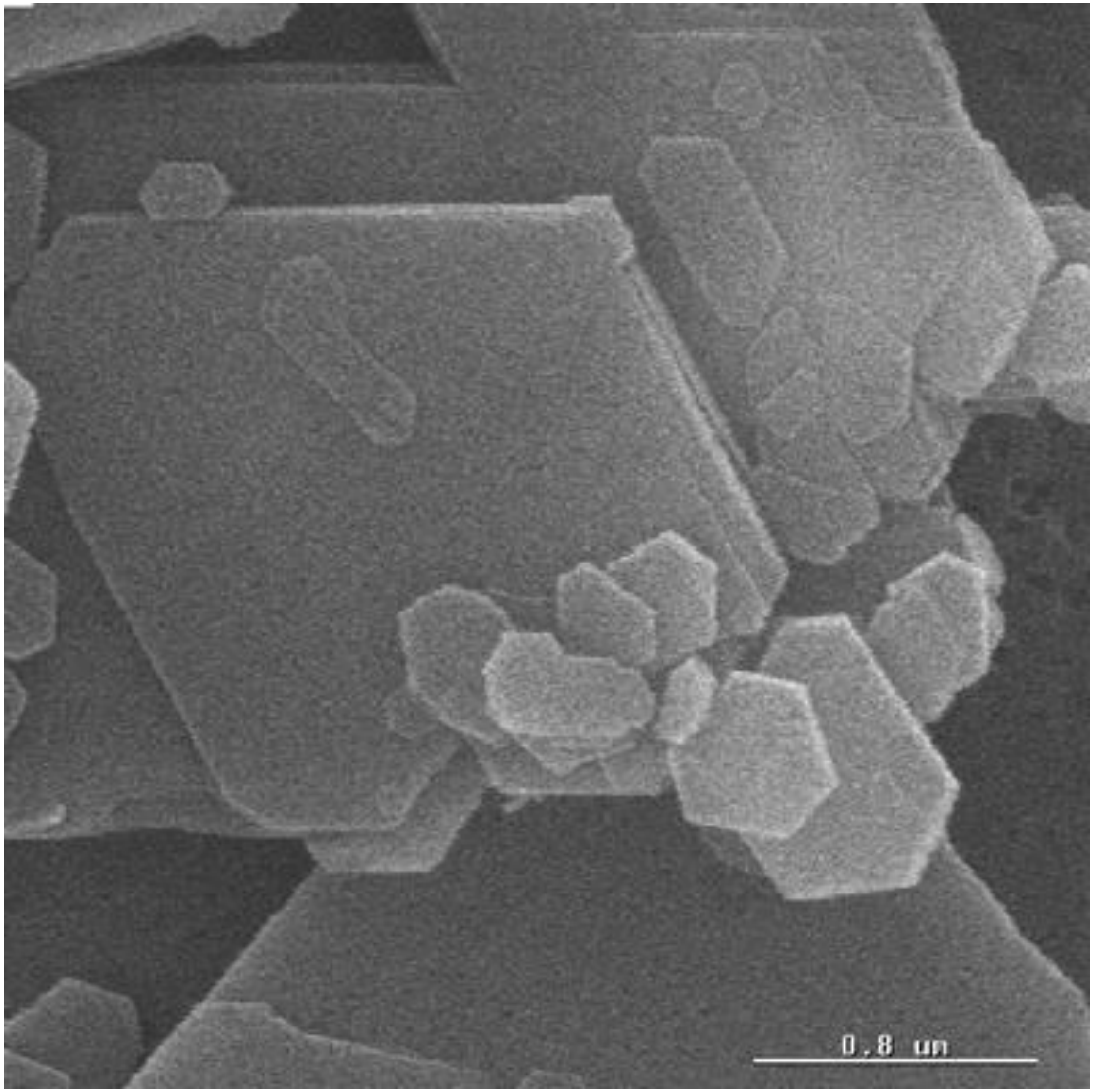
$KAl_2(Si_3Al)O_{10}(OH)_2$

In brittle micas, interlayer ions are divalent, like Ca^{2+}
Because of 2+ charge, they are stronger than True micas. These micas are rare.



This tabulation giving the layer by layer population of elements correlates with the doubled formula $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$.

Mica



Mullite

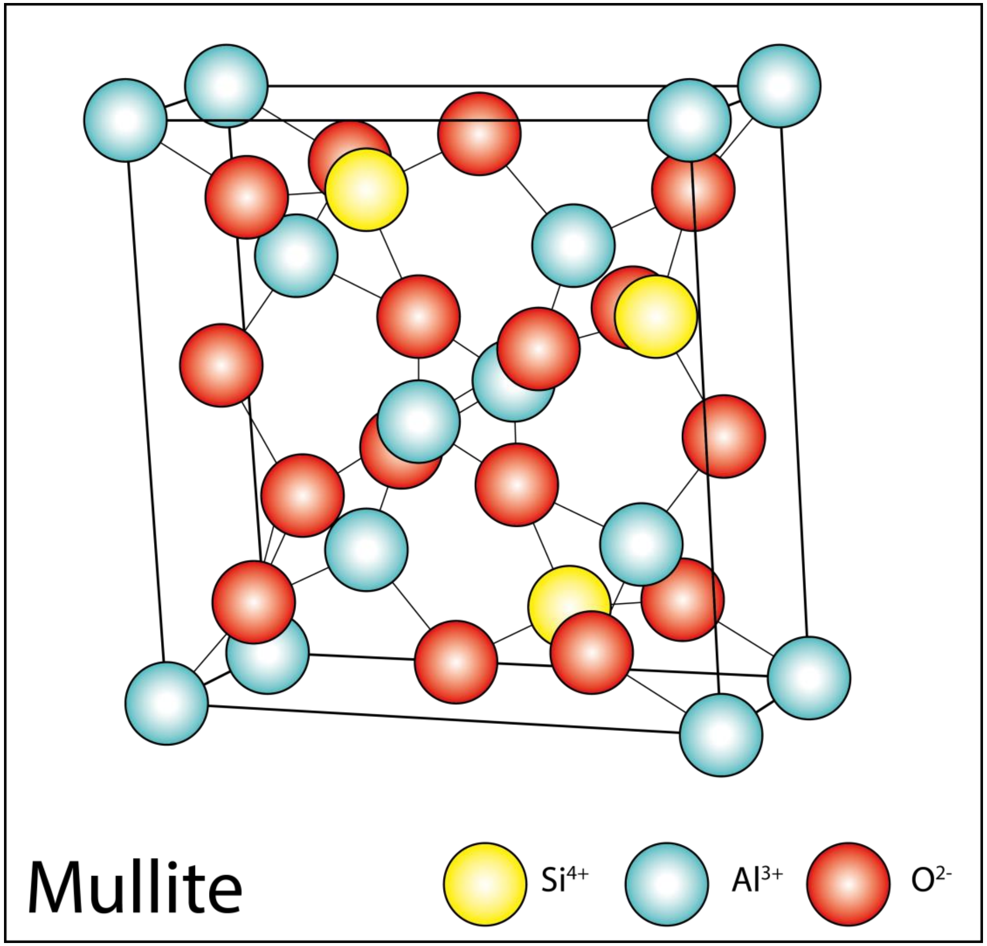
Mullite has the formula of $3Al_2O_3{\cdot}2SiO_2$ and exist in nature very rare. Mullite is suitable for high temperature applications. It is used in furnace lining, refractory applications in iron, steel and glass industries.

Can be produced;

- By sintering mixture of kyanite (Al_2OSiO_4), bauxite ($Al(OH)_3$) and kaolin. Sintered at around 1600^0C with correct proportions. Sintered product contains around 60-70% mullite. Rest will be silica based by products.
- By fusing in an electric arc furnace at about 1750^0C of alumina and kaolin. This method gives higher purity mullite ($>95\%$)

It has a high melting point, around 1840^0C

Mullite



Alumina, Al_2O_3

Alumina is known as corundum, which is the name of its crystal structure. It is produced mainly from Bauxite ($Al(OH)_3$) mineral by Bayer process. Bauxite has some impurities of iron, titanium and silicon oxide impurities in it.

A purity of 95% alumina, with main impurity of Na_2O, can be obtained by Bayer process.

1- Groung bauxite is treated with NaOH solution at $\sim 150^0$C. The impurities in bauxite do not dissolve.

$$Al(OH)_{3(s)} + NaOH_{(aq)} = Na^+_{(aq)} + Al(OH)_4{}^-{}_{(aq)}$$

2- By filtration, we get rid of impurities. To the filtered solution, gibbsite crystals are added as seeds for the ppt of Al-hydrate from the solution.

Alumina, Al_2O_3

3- The ppts are separated from the solution by filtration. Then washed to get rid of residual sodium.

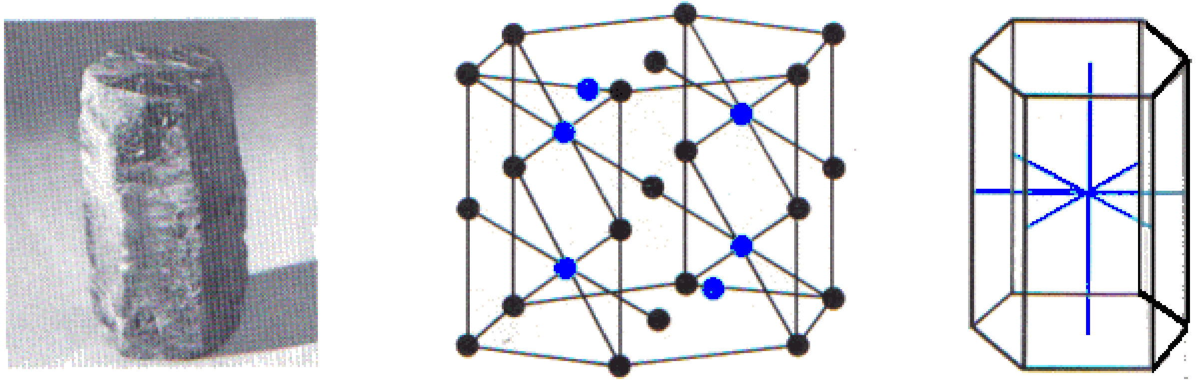
4- Calcination of aluminium hydroxite at around 1100^0C-1200^0C.

$$2Al(OH)_{3(s)}=Al_2O_{3\ (s)}+H_2O_{\ (g)}$$

5- 5-10 μm crystals produced. Further milling is done to decrease particle size. Purity is >99.5%, main impurity is Na_2O

Alumina, Al_2O_3

Its crystal structure is corundum, in an hexagonal lattice.



Alumina has melting temperature of 2072^0C.

Magnesium Oxide, MgO

It is found in the form of periclase mineral. But, it is not used as MgO source, because it is rare in nature.

MgO sources are mainly magnesium hydroxide ($Mg(OH)$) or magnesite ($MgCO_3$, magnesium carbonate). Impurities in magnesite mineral are quartz, talc ($Mg_3Si_4O_{10}(OH)_2$), mica, and magnetite (Fe_3O_4)

Beneficiation is applied to get rid of impurities include crushing, screening, washing, magnetic separation, froth flotation. After that;

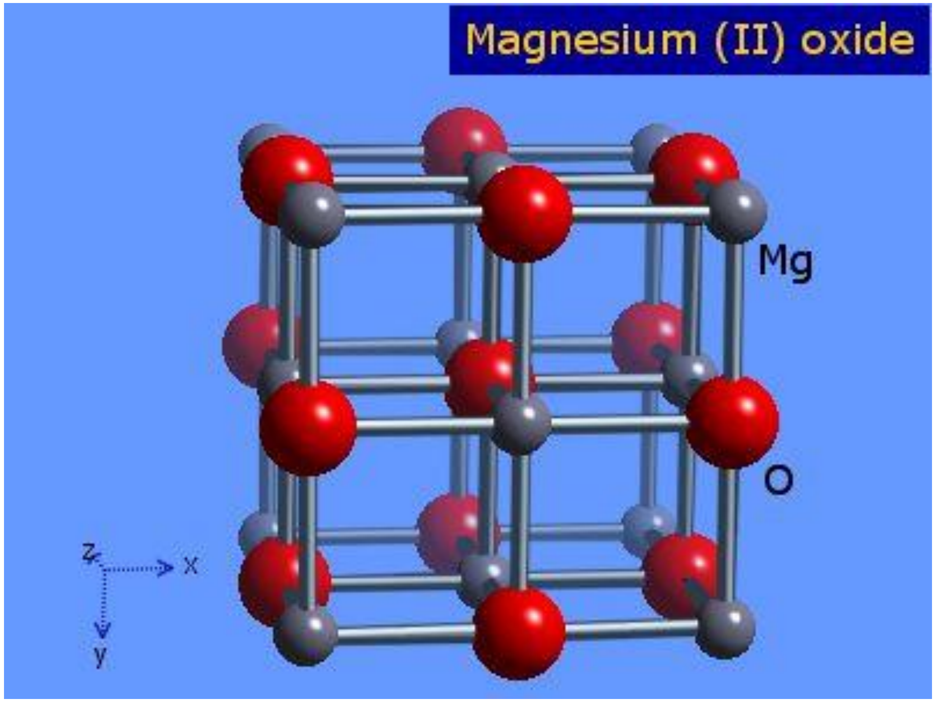
$$MgCO_3 = MgO + CO_2 \text{ calcination @ } 800^0C\text{-}900^0C$$

MgO is also produced from seawater. 1,3 gr MgO is present in 1 kg seawater.

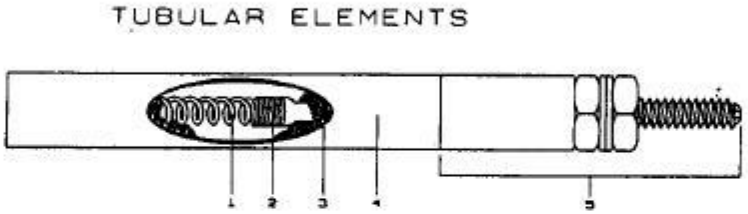
Most of MgO is used as refractory linings in furnaces.

Magnesium Oxide, MgO

MgO has Rock Salt Structure



Magnesium Oxide, MgO



Where: 1 - Element Coil
2 - Element Cold Junction
3 - Magnesium Oxide (MgO)
4 - Element Sheath
5 - Element Terminal Post

Zirconia, ZrO_2

Source of ZrO_2 is Zircon ($ZrSiO_4$), present in volcanic rocks.

Secondary source is beach-sands. Mainly in Australia and Brazil. In Turkey, Şile beach has also Zircon concentration around 3%.

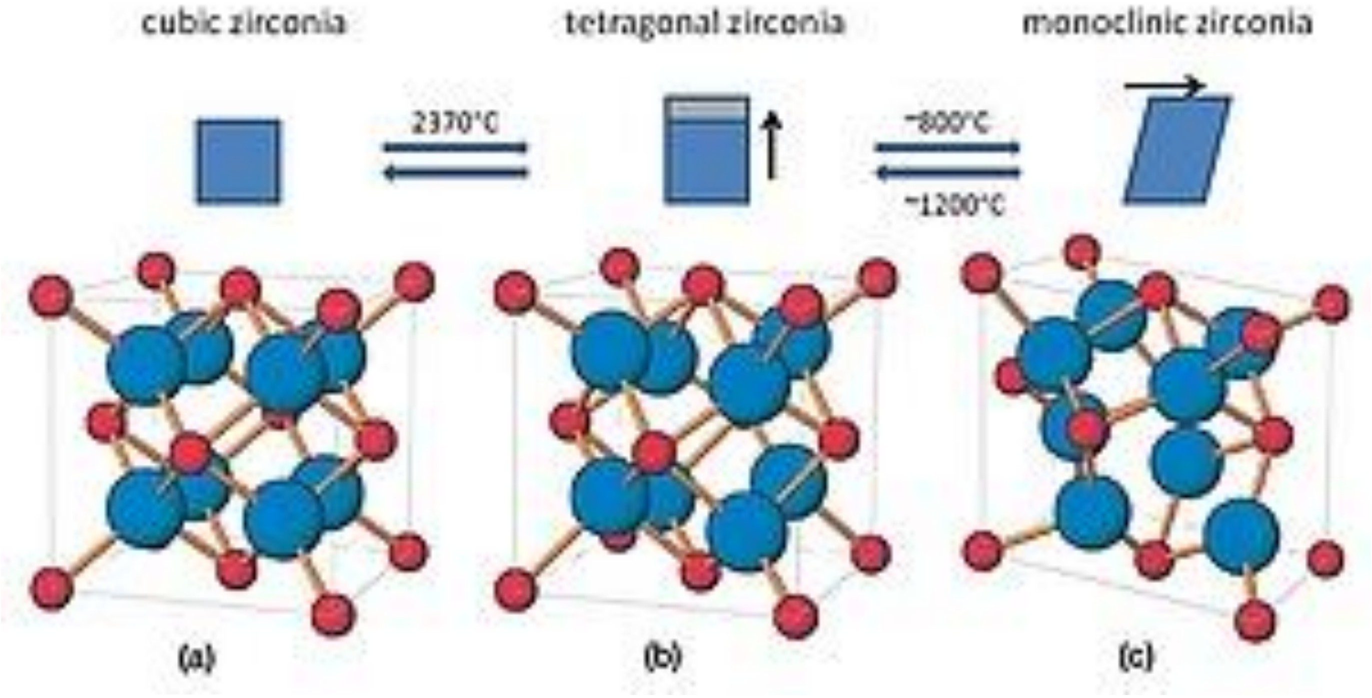
One way of Zirconia production is dissociating zircon above 1750^0C with the help of plasma.

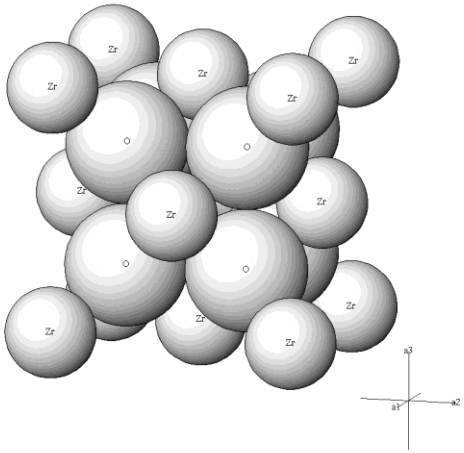
$$ZrSiO_4 = ZrO_2 + SiO_2$$

During cooling, zirconia solidifies first. Later, silica solidifies and covers zirconia crystals. At high cooling rates, silica forms glass. This can be separated from zirconia by dissolving it in hot NaOH.

Another method is direct melting of zircon in electric arc furnace at 2300^0C. At this T Silica melts and it can be separated from solid state zirconia.

Zirconia, ZrO_2





Pure zirconium dioxide undergoes a phase transformation from monoclinic (stable at the room temperature) to tetragonal (at about 1173 °C) and then to cubic (at about 2370 °C)

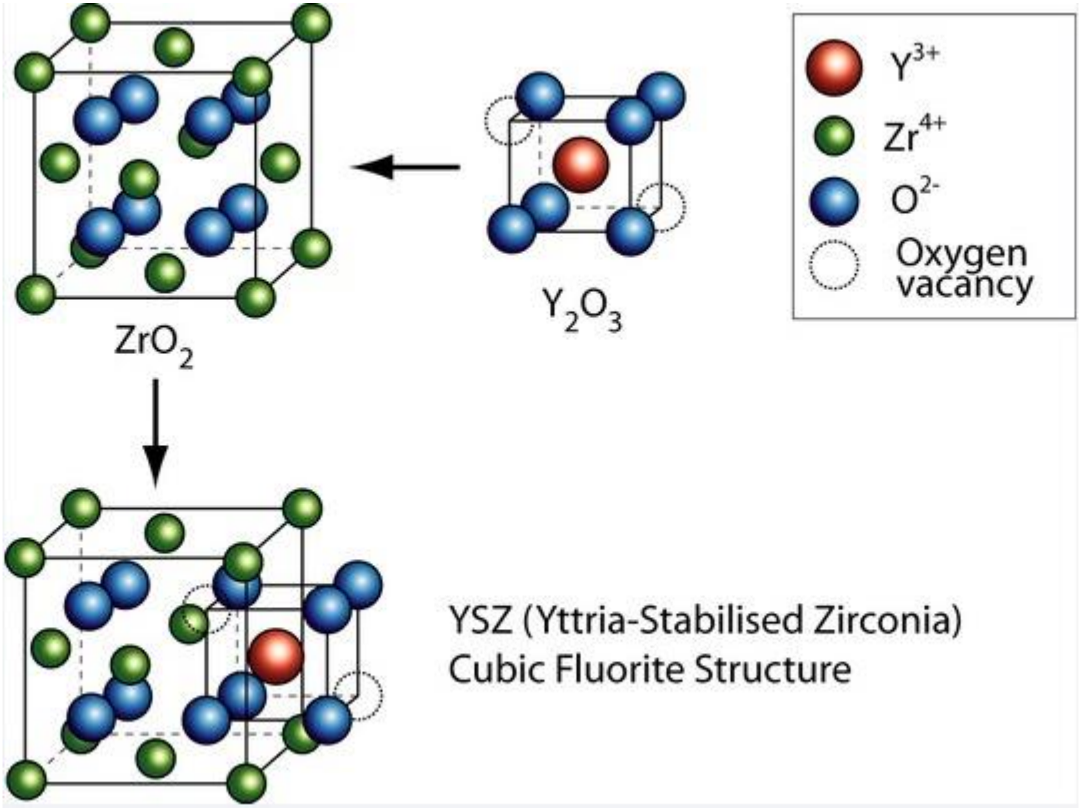
Zirconia, ZrO_2

Pure zirconium dioxide undergoes a phase transformation from monoclinic (stable at the room temperature) to tetragonal (at about 1173 °C) and then to cubic (at about 2370 °C)

monoclinic (1173 °C) ↔ tetragonal (2370 °C) ↔ cubic (2690 °C) ↔ melt

Stable sintered zirconia ceramic products is difficult because of the large volume change from tetragonal to monoclinic (~ 9%). Stabilization of the cubic polymorph of zirconia over wider range of temperatures is accomplished by substitution of some of the Zr^{4+} ions (ionic radius of 0.82 Å, too small for ideal lattice of fluorite characteristic for the tetragonal zirconia) in the crystal lattice with slightly larger ions, e.g., those of Y^{3+} (ionic radius of 0.96 Å). The resulting doped zirconia materials are termed *stabilized zirconia*

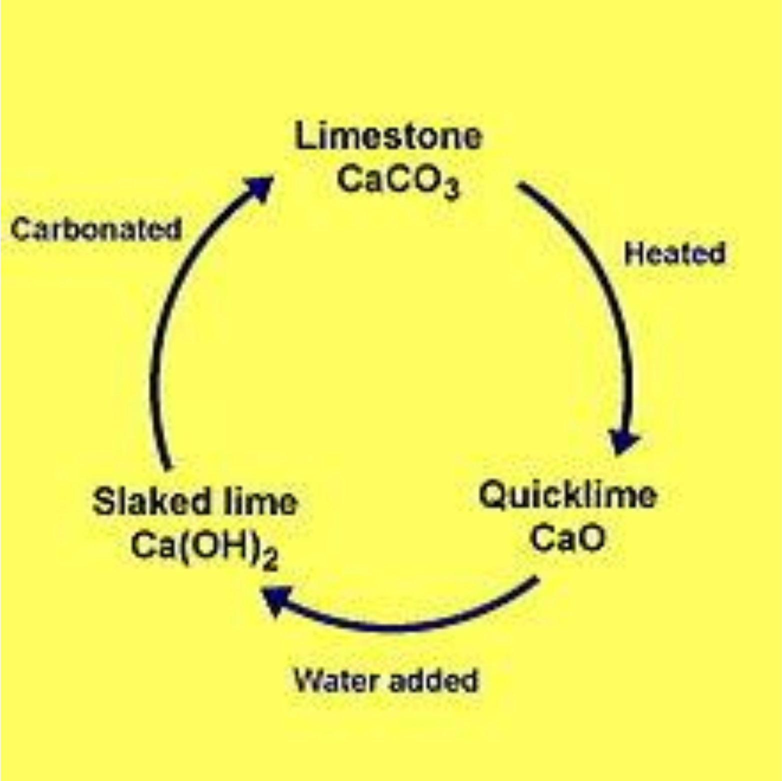
Zirconia, ZrO_2



Stabilization with yttria, forms oxygen vacancy, which brings oxygen ion conductivity to material.

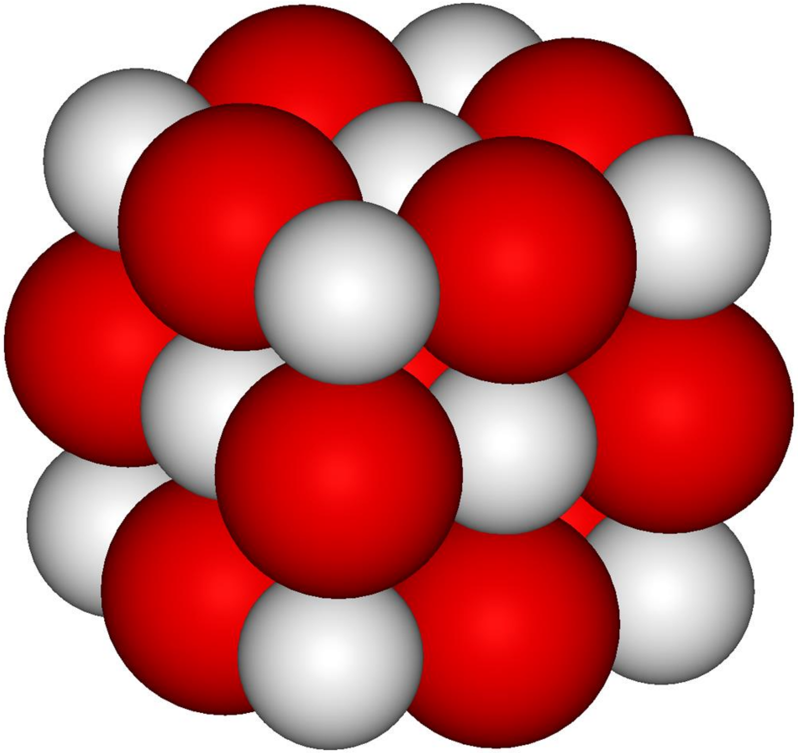
Calcium Oxide, CaO

CaO – Calcium Oxide	- Lime, Quicklime
$Ca(OH)_2$ – Calcium Hydroxide	- Lime, Slaked lime
$CaCO_3$ – Calcium Carbonate	- Calcite, Limestone



Calcium Oxide, CaO

Rock Salt Structure, similar to MgO

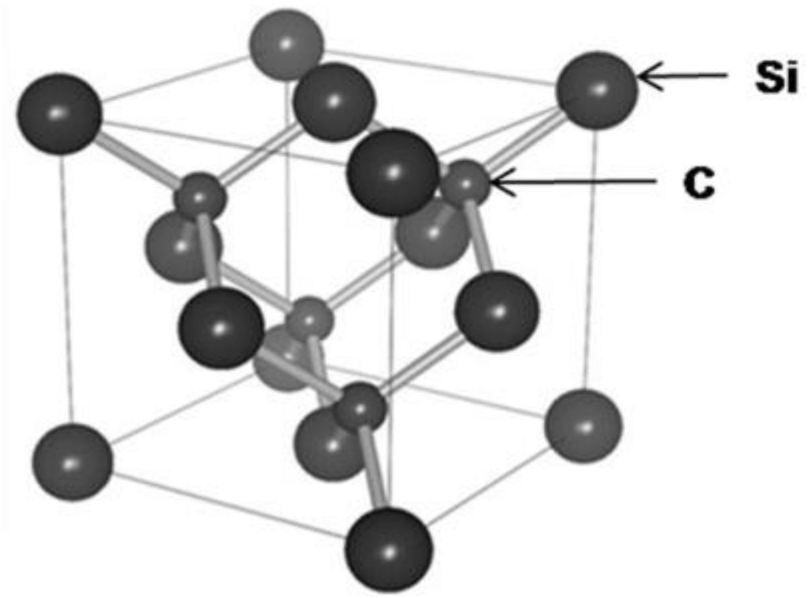


SiC

Silicon Carbide, one of the non-oxide ceramics.

- One of the hardest material (after diamond)
- Possess very high thermal conductivity
- High electrical conductivity

- Crystal structure is : Diamond Cubic



Graphite

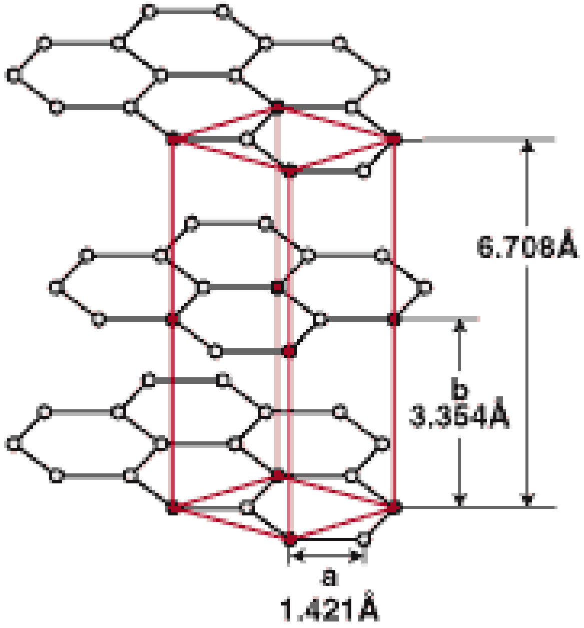
One of the crystalline forms of carbon.

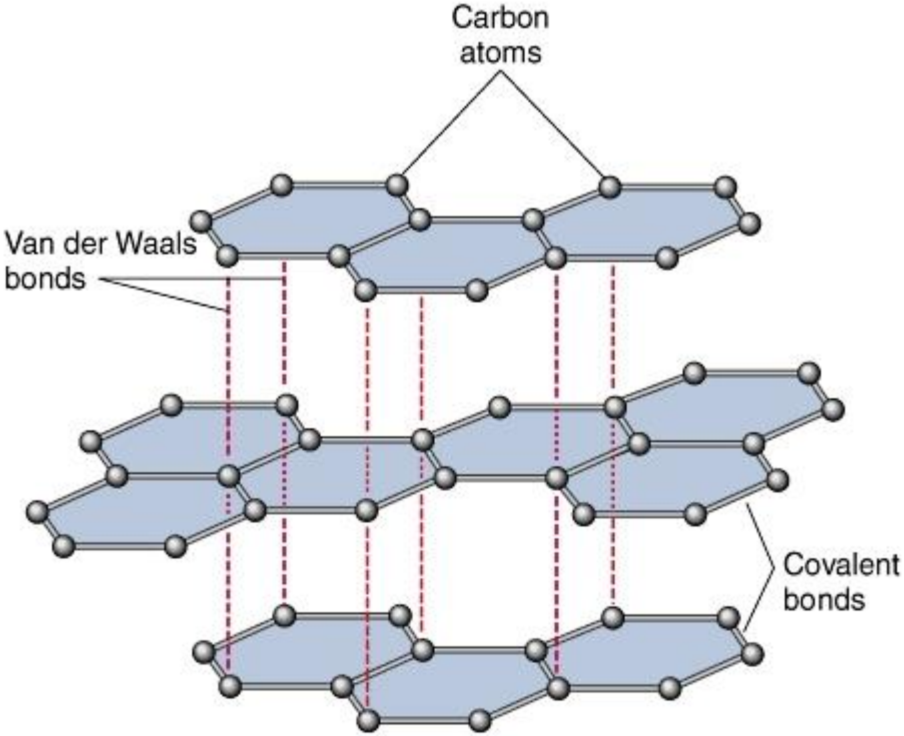
Graphite has very high melting point (~4000^{0}C), but it burns out at 600^{0}C in O_2 atm.

- Extremely soft material because of the sheet-structure and van der Waals bonding btw sheets.
- Extremely high thermal conductivity in a-axis
- Very low thermal conductivity in c-axis
- High electrical conductivity in a-axis. Graphite electrodes used in arc furnaces.

Natural graphites are used as refractor

- Crystal structure is hexagonal





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