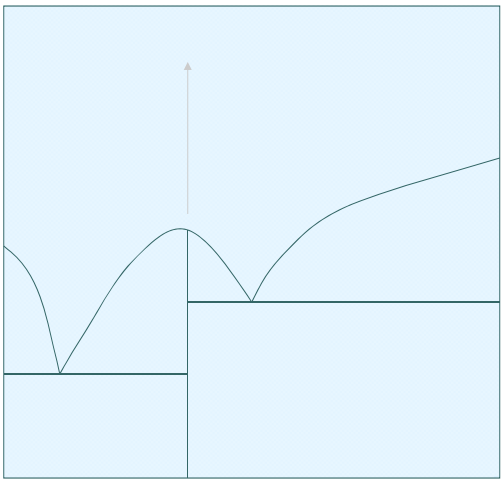
Binary system with Compound Formation



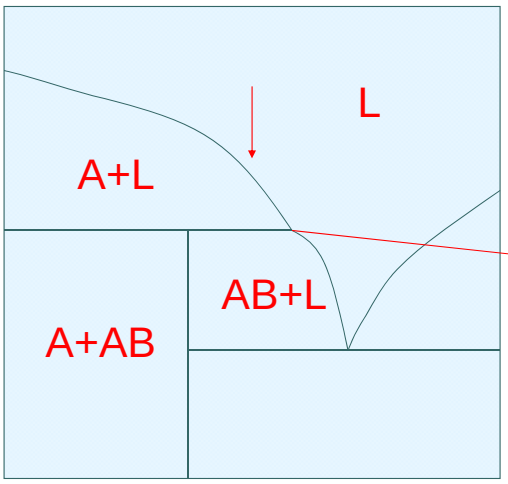
A AB B

AB melts congruently

Simple eutectic systems

Chem 253, UC, Berkeley

Binary system with Compound Formation



A AB B

AB melts incongruently

A, AB, Liquid

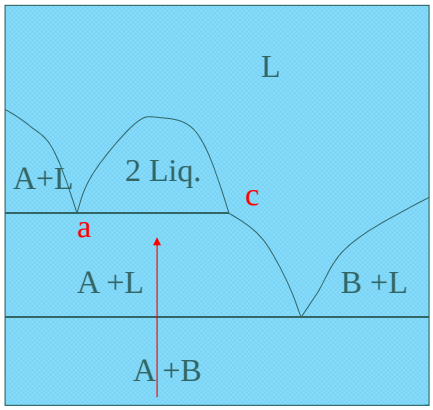
Peritectic point

invariant point

Binary Systems with Immiscible Liquids

Immiscible dome: two liquid phase coexist

P+F=C+1



Point a:

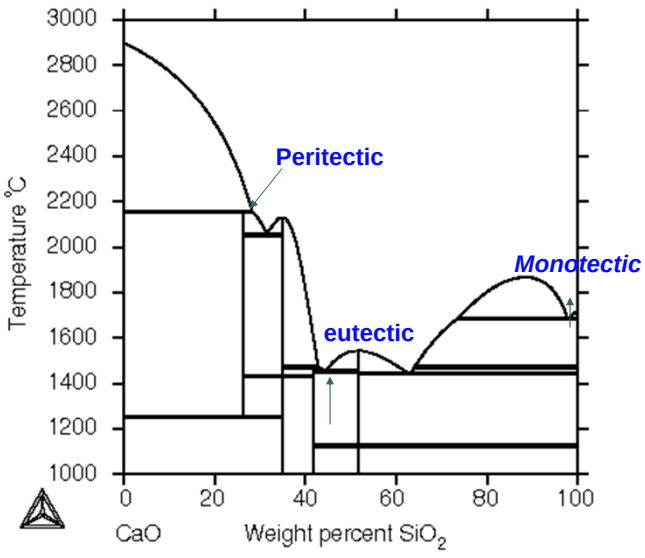
Liq. a, Liq. c
Crystal A

P=3 C=2

F=0

Monotectic

invariant point



invariant point

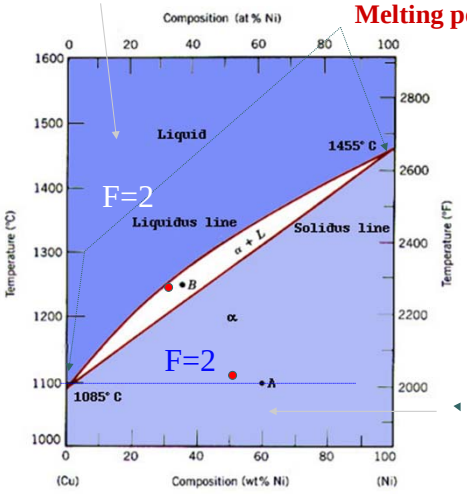
W. Callister Chapter9
Mater. Sci. Eng. An introduction

Binary Isomorphous System

Binary system with solid solution

Mutually soluble in liquid state

Melting points



α-phase is substitutional solid consisting of both Cu and Ni and having an FCC structure

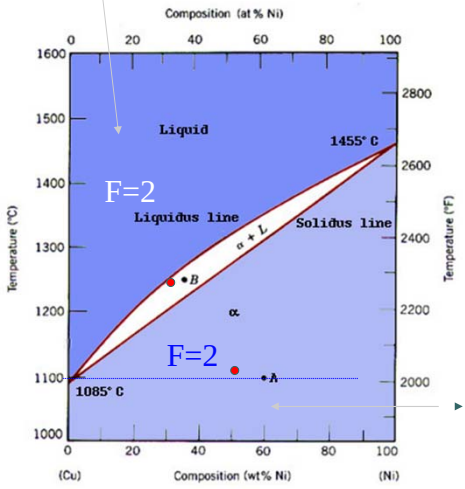
- atoms have similar radii;
- both pure materials have same crystal structure;
- similar electronegativity (otherwise may form a compound instead);

Mutually soluble in solid State

Chem 253, UC, Berkeley

Binary Isomorphous System

Mutually soluble in liquid state



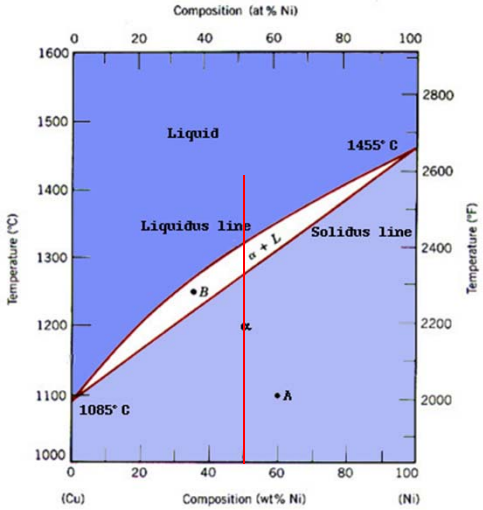
P+F=C+1

Phase present

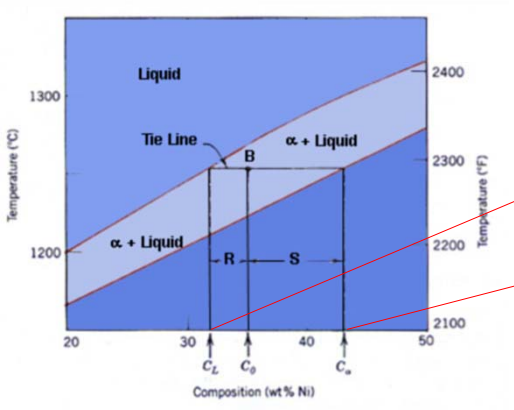
- **Point A - α**
- **Point B - α + L**

Mutually soluble in solid State

A 50%-50% composition begins melting at about 1280 °C; the amount of the liquid phase continuously increases with temperature until about 1320 °C where the alloy is completely liquid.



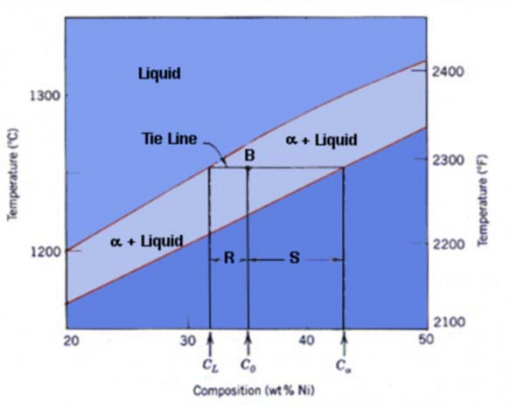
Example: 35 wt% Ni – 65 wt% Cu alloy at 1250 °C



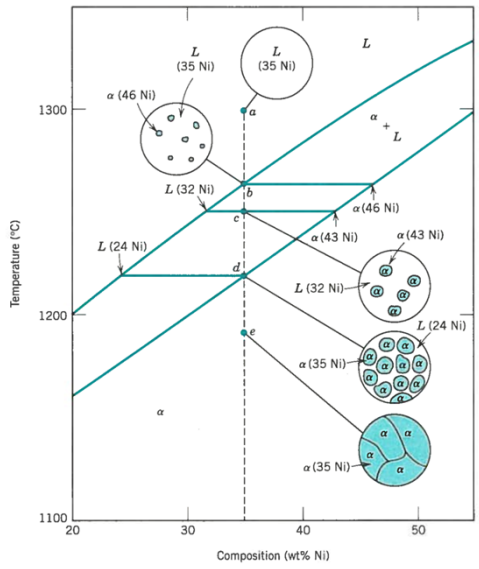
Point B

- α + L region
- Liquid phase (31.5 wt% Ni – 68.5 wt % Cu)
- Solid phase (42.5 wt % Ni – 57.5 wt % Cu)

Example



- T = 1250 ^{0}C; α + L; 35 wt % Ni – 65 wt % Cu
- Compute % α and % L
- C_o = 35, C_L = 31.5, C_α = 42.5
- $W_L = \frac{42.5 - 35}{42.5 - 31.5}$ = 0.68 (68 wt %)
- $W_\alpha = \frac{35 - 31.5}{42.5 - 31.5}$ = 0.32 (32 wt %)



No microstructural changes until reach liquidus line.

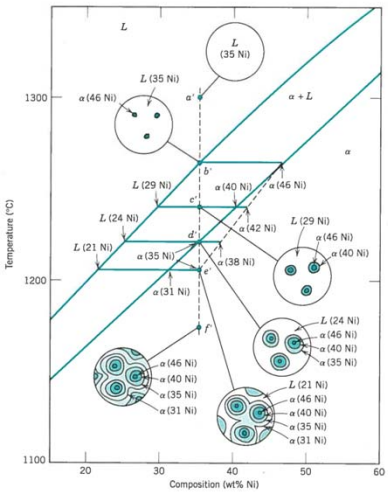
b – composition dictated by tie line intersection of liquidus and solidus.

Note: overall alloy composition remains the same but phase compositions change as cooling occurs.

c – from b to c α-phase increases as dictated by lever rule and composition changes as dictated by tie lines and their intersection with solidus/liquidus.

Equilibrium solidification requires very slow cooling!

Non-equilibrium solidification



Compositional changes as defined by boundaries requires readjustment via diffusion over time – non-equilibrium.

Diffusion is especially low in solids – much higher in liquids and decreases with temperature Decrease.

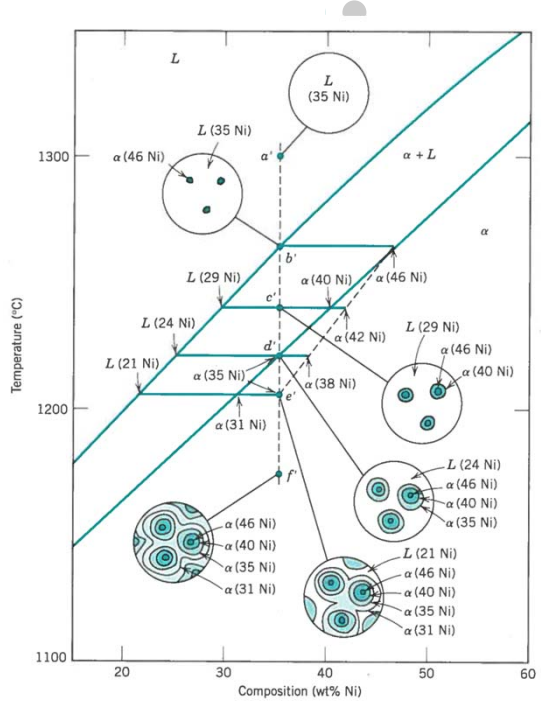
Note for dashed line shown no phase change until Pt. b'.

Pt. c' – composition dictated by tie-lines as shown; but α-phase has not had time to change from 46% Pb to 40% Ni – reasonable average is 42%.

Note similar situation at pt. d'.

Result is a constant liquidus line (due to much more freedom of movement and much higher diffusion; shifted solidus line (dashed) due to diffusion.

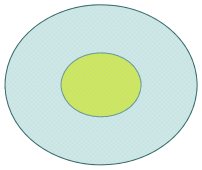
Pt. d' - should be complete solidification, but effects of diffusion dominate.



Consequences of non-equilibrium solidification:

- **segregation, cored structure;**
- **upon reheating – grain boundaries will melt first causing loss of structural integrity.**

Fractional Crystallization

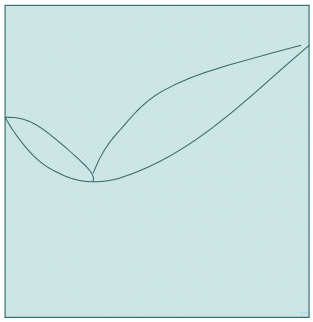


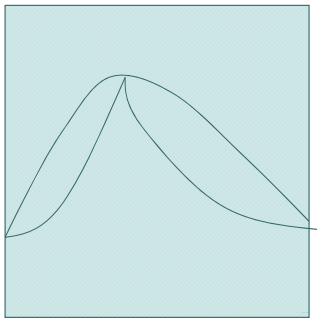
CaAl2Si2O8 NaAlSi3O8

Crystallization

- **Very slow cooling rate: crystallization to the same composition**
- **Slightly faster: Fractional crystallization**
- **Very fast: no time for any crystallization, form glass**

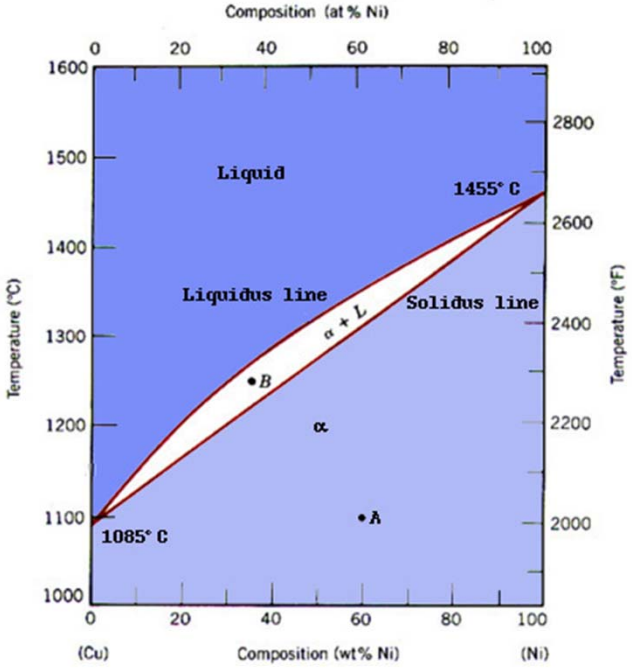
Binary solid solution with thermal minima or maxima





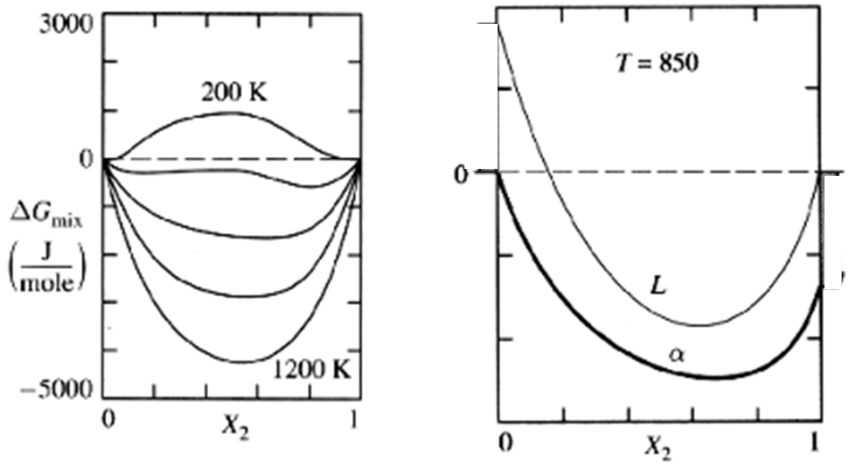
Indifferent point, NOT invariant point

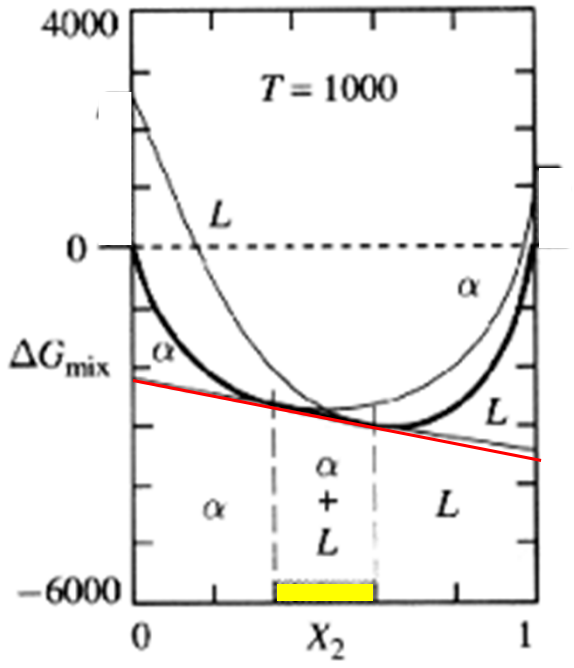
There are NEVER three phases.

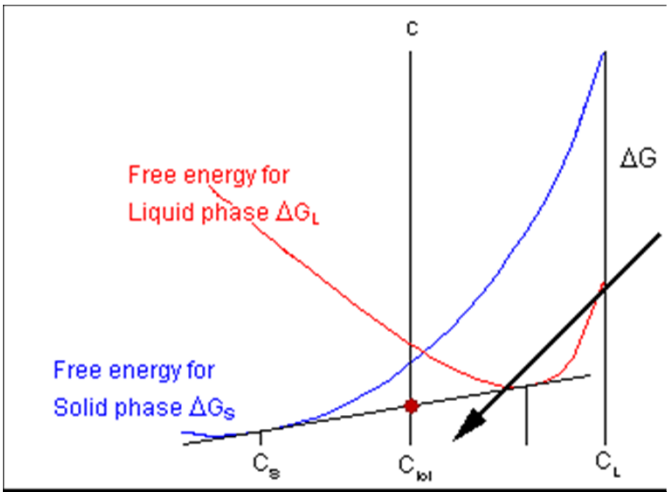


Common Tangent Construction of Phase Diagrams

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

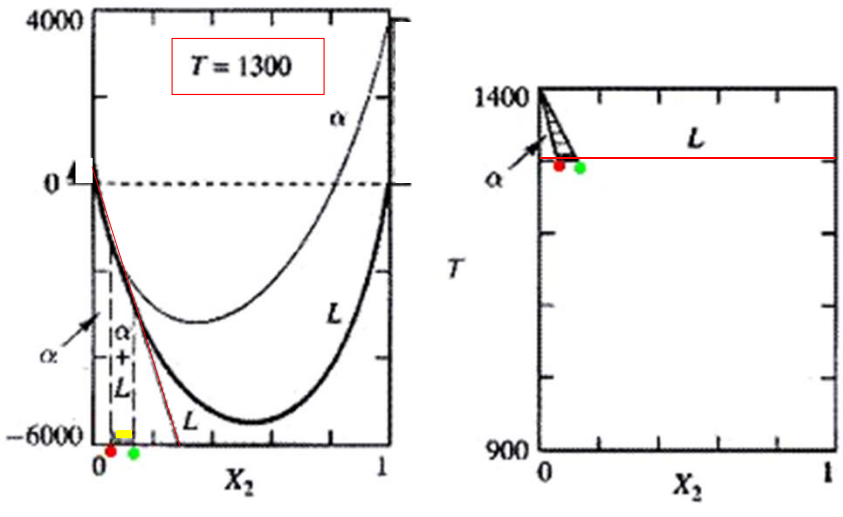


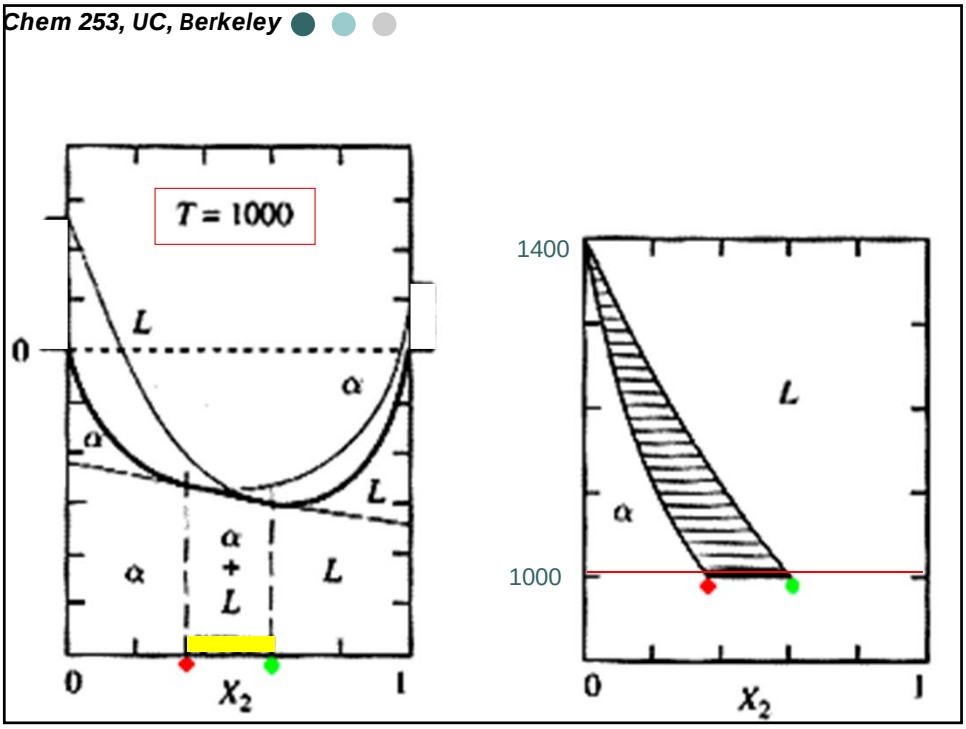




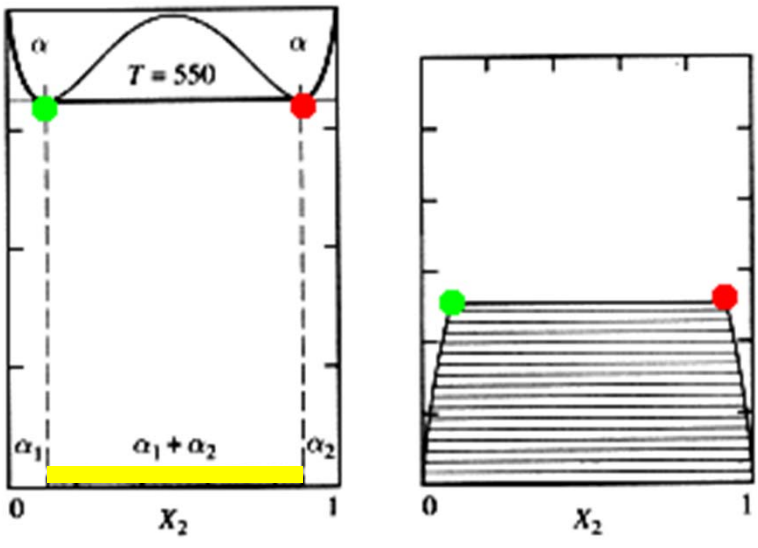
- The common tangent construction can be seen linking the solid and liquid free energy curves to minimize the system's overall free energy for a given overall composition.
- This construction also identifies the composition of the solid and liquid phases which are in equilibrium at this temperature.

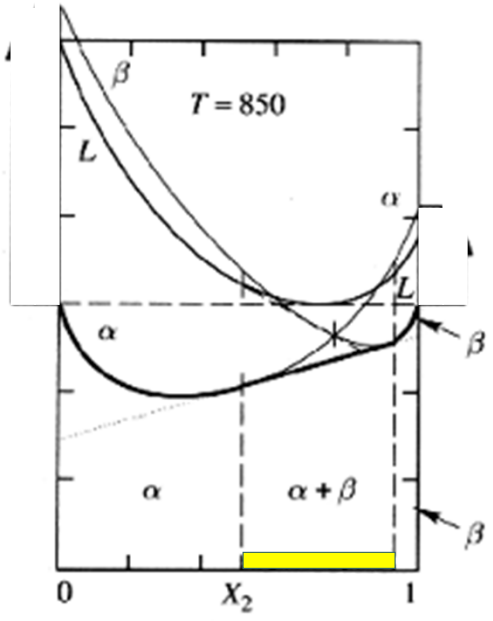
Chem 253, UC, Berkeley

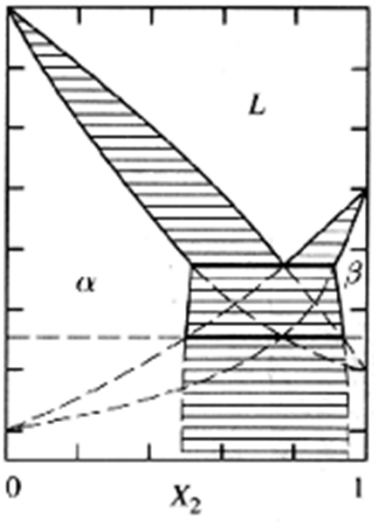




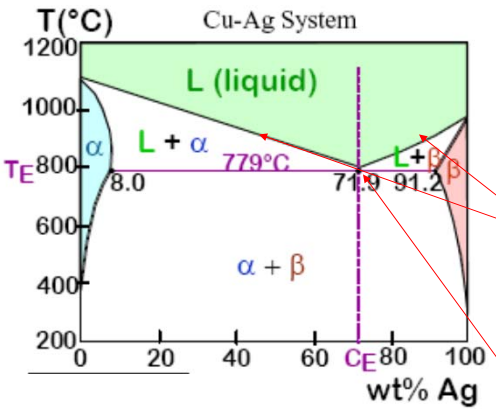
Miscibility gap



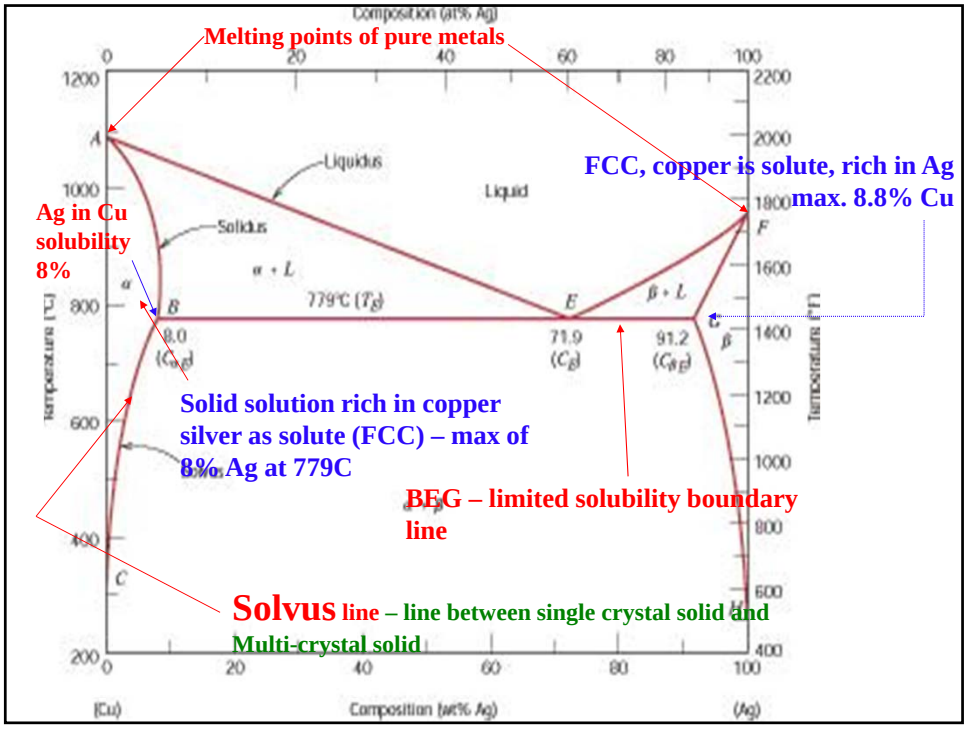




Binary eutectic system with partial solution formation

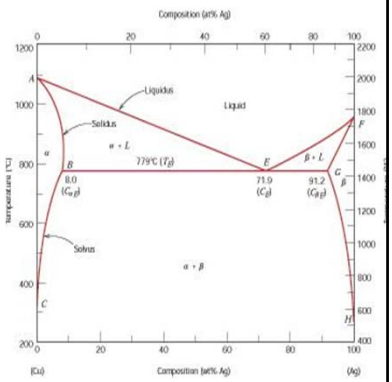


- Three – two phase regions α + L, β + L, and α + β
- Compositions and relative amounts for the phases may be determined using lever rule.
- Liquidus line - melting temperature lowered by adding Ag to Cu (vice versa).
- Point E – invariant point



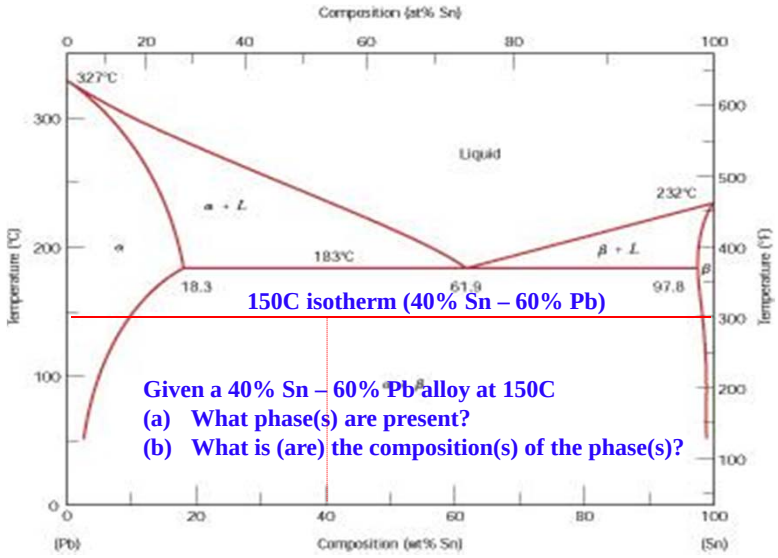
Chem 253, UC, Berkeley

Eutectic isotherm

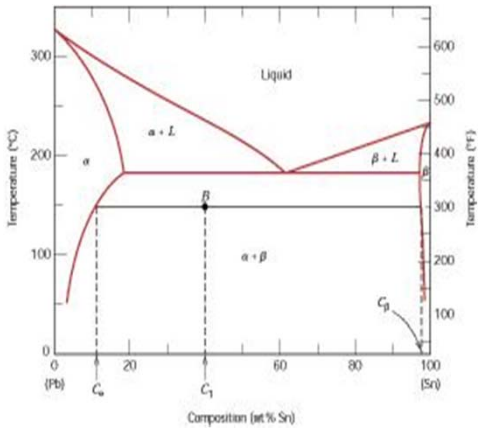


- $L\ (C_E) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha\ (C_{\alpha E}) + \beta(C_{\beta E})$
- **Eutectic reaction**

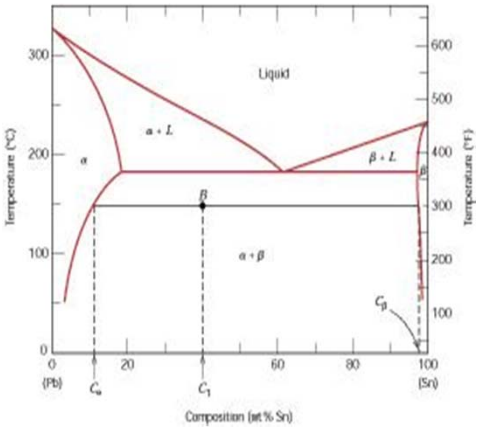
$$L\ (71.9\ \text{wt \% Ag}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha\ (8.0\ \text{wt \% Ag}) + \beta(91.2\ \text{wt \% Ag})$$



Given a 40% Sn – 60% Pb alloy at 150C
(a) What phase(s) are present?
(b) What is (are) the composition(s) of the phase(s)?



- **40 wt % Sn – 60 wt % Pb alloy at 150^{0}C**
- **Phase present**
  - **Temperature – composition point in α + β region (α and β will coexist)**
  - **C $_\alpha$ (10 wt % Sn – 90 wt % Pb)**
  - **C $_\beta$ (98 wt % Sn – 2 wt % Pb)**



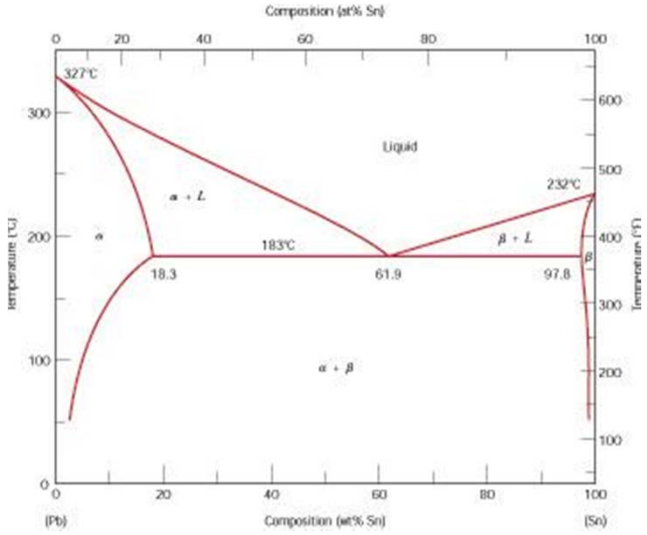
Relative amounts of each phase (weight)

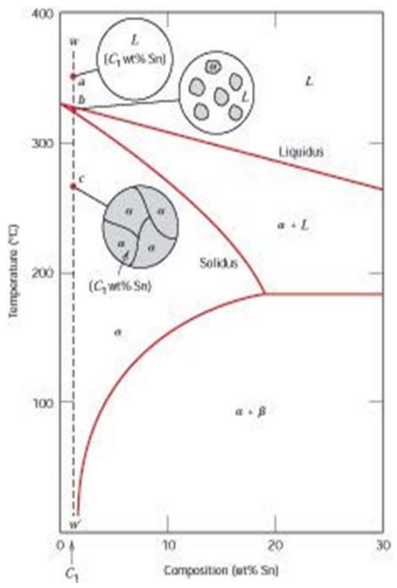
$$W_\alpha = \frac{C_\beta - C_1}{C_\beta - C_\alpha} = \frac{98-40}{98-10} = 0.66$$

$$W_\beta = \frac{C_1 - C_\alpha}{C_\beta - C_\alpha} = \frac{40-10}{98-10} = 0.34$$

Lever rule

The microstructural changes that occur in eutectic binary diagram

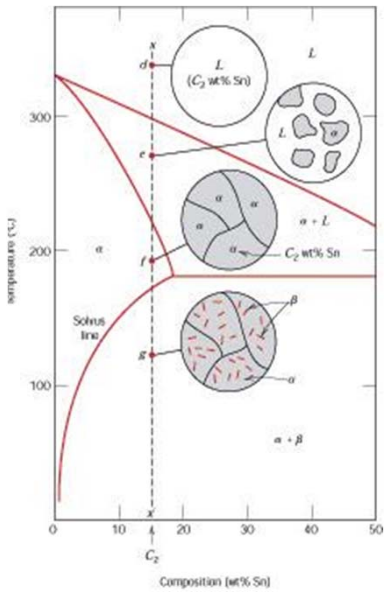




Pure element to maximum solubility at room temperature:

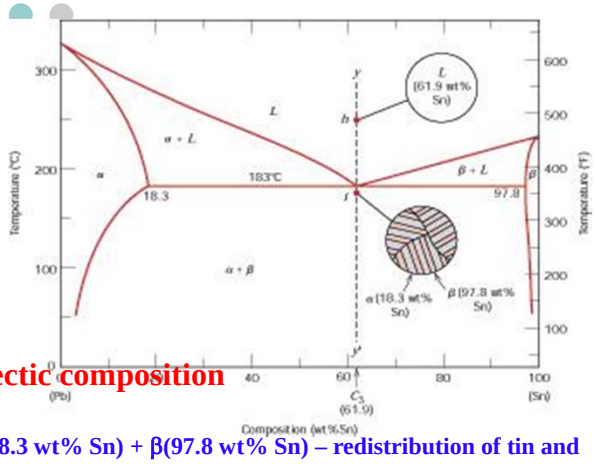
- **Alloy is liquid until it passes through liquidus, α-phase begins to form**
- **More α is formed while passing into L+ α region –compositional differences dictated by tie lines and boundaries**
- **Result in polycrystal with uniform composition**
- **Note crystal maintains α-structure all the way to room temperatures (under equilibrium).**

Chem 253, UC, Berkeley



Composition range between room temperature solubility and max. solid solubility at eutectic temperature:

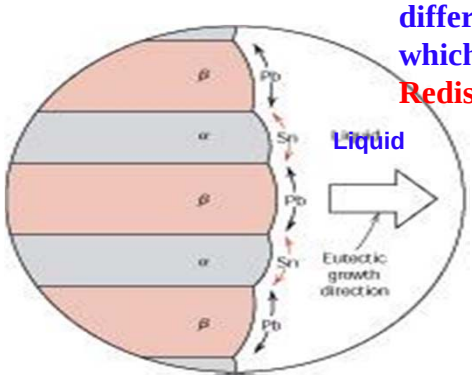
- **Changes are similar to previous case as we move to solvus line.**
- **Just above solvus line, pt. f, microstructure consists of grains with composition C_2.**
- **Upon crossing the solvus line, the α solid solubility is exceeded – formation of β phase particles.**
- **With continued cooling, β particles will continue to grow in size because the mass fraction of β increases slightly with decreasing temperature.**



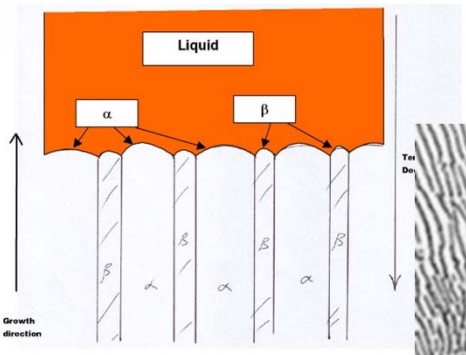
Solidification of eutectic composition

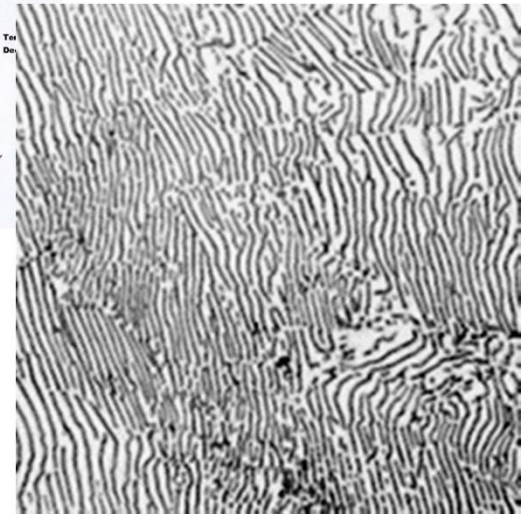
- L(61.9 wt% Sn) ⇄ α(18.3 wt% Sn) + β(97.8 wt% Sn) – redistribution of tin and lead at eutectic temperature.
- Redistribution is accomplished by diffusion – microstructure is lamellae or columnar structure.
- This lamellae/columnar configuration: atomic diffusion of lead and tin need only occur over relatively short distances.

During the eutectic transformation from liquid to solid (α + β), a redistribution of Pb and Sn is necessary because and α and β have different compositions neither of which is the same as the liquid. Redistribution is through diffusion.



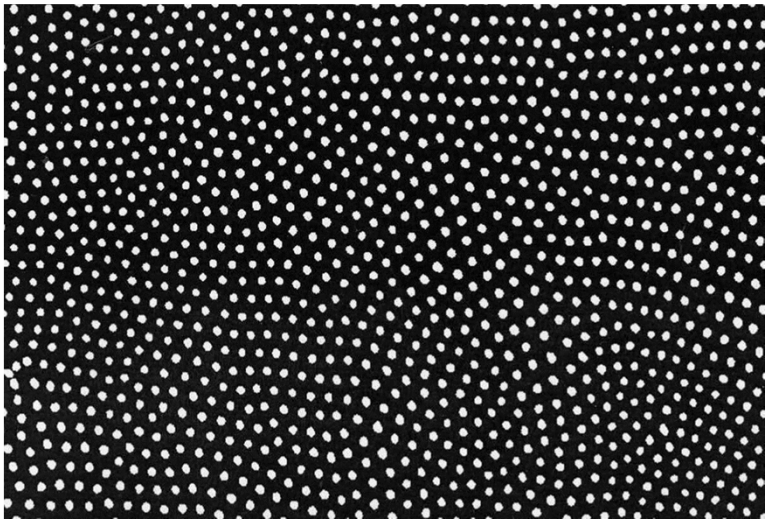
Pb atoms diffuse toward α-phase since it is lead-rich (81.7%); Sn atoms diffuse toward β-phase since it is tin rich (97.8%)

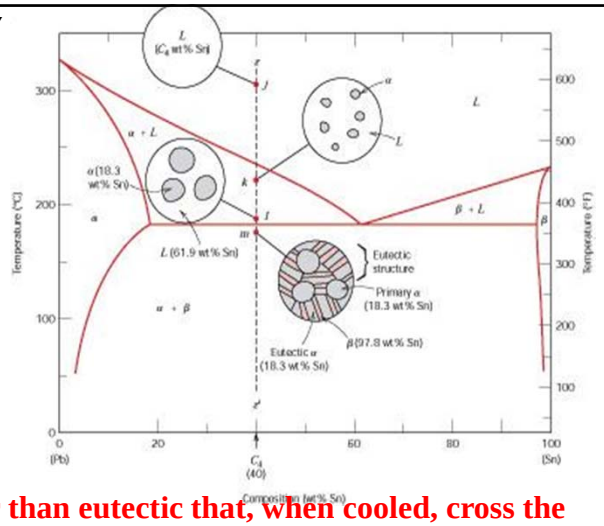




Lamellae structure

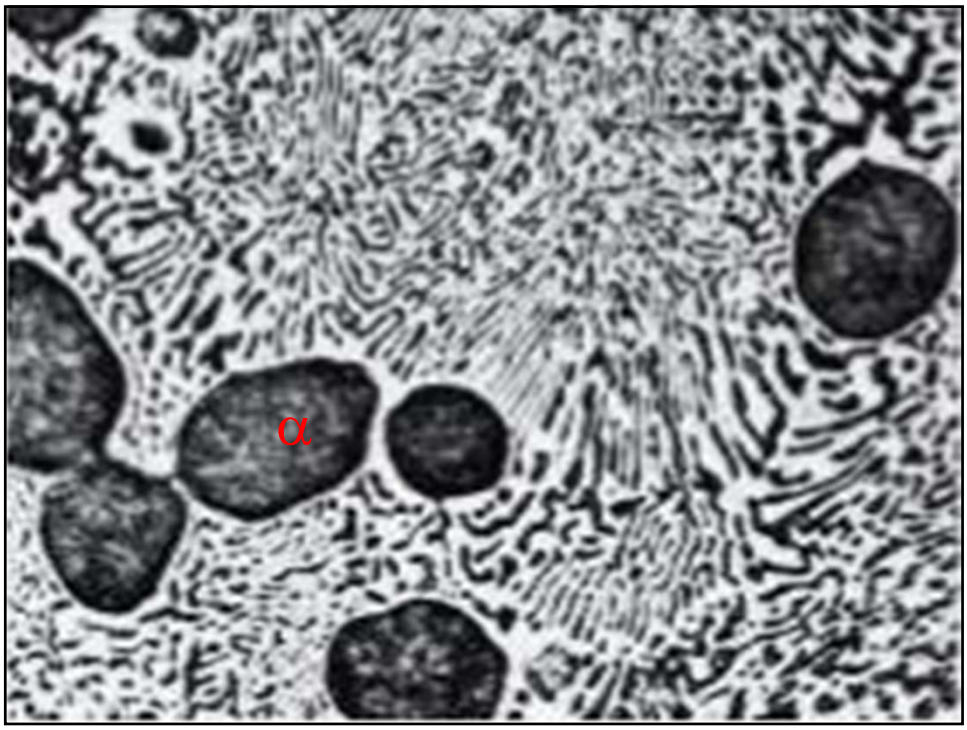
Columnar structure

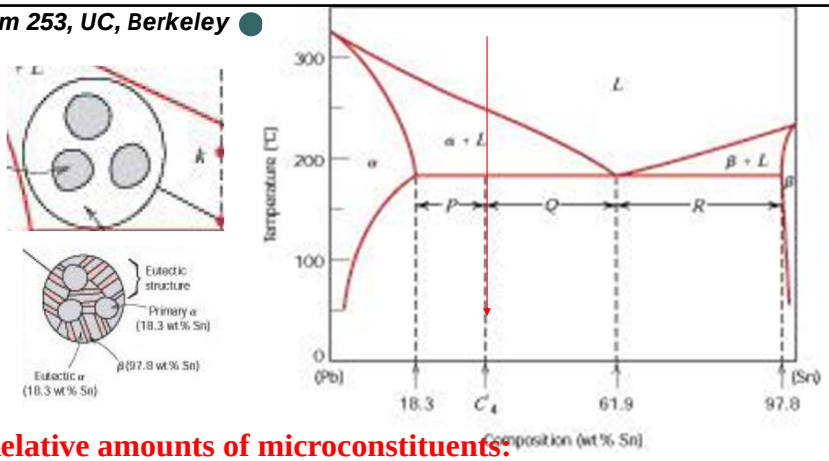




Compositions other than eutectic that, when cooled, cross the eutectic temperature:

As eutectic temperature line is crossed, liquid phase, which is of the eutectic composition – follow boundary line – will transform to eutectic structure (lamellae).





Relative amounts of microconstituents:

Eutectic microconstituent, W_e = same as liquid phase from which it was transformed, W_L
$W_e = W_L = P/(P + Q) = (C_4' - 18.3)/(61.9 - 18.3)$

Primary microconstitutent, $W_{\alpha'} = Q/(P + Q) = (61.9 - C_4')/(61.9 - 18.3)$

Fraction of total $\alpha = W_\alpha = (Q + R)/(P + Q + R) = (C_4' - 18.3)/(97.8 - 18.3)$

ADVANCED MATERIALS

DOI: 10.1002/adma.200700726

Well-Aligned Nanocylinder Formation in Phase-Separated Metal-Silicide–Silicon and Metal-Germanide–Germanium Systems

By *Nobuhiro Yasui*, *Ryoko Horie*, *Yoshihiro Ohashi*, *Koichi Tanji*, and *Tohru Den**

Table 1. List of the examined materials and their eutectic temperatures

Materials [silicide]	Eutectic Temperature [°C]	Materials [germanide]	Eutectic Temperature [°C]
Al-Si [11,18]	577	Al-Ge [12, 18]	420
Cu_3Si-Si [18]	802	Cu_3Ge-Ge [18]	644
Pd_2Si-Si [19]	825	Ag-Ge [18]	651
$NiSi_2$-Si [20]	960	$Mn_{11}Ge_8$-Ge [28]	720
PtSi-Si [18]	979	PdGe-Ge [18]	725
RhSi-Si [21]	1060	NiGe-Ge [18]	762
$Mn_{11}Si_{19}$-Si [18]	1142	$PtGe_2$-Ge [18]	802
$FeSi_2$-Si [18]	1207	$Co_{0.875}Ge_2$-Ge [18]	810
$IrSi_3$-Si [22]	1221	Rh_5Ge_4-Ge [18]	850
$CoSi_2$-Si [18]	1259	$Cr_{11}Ge_{19}$-Ge [18]	895
$NbSi_2$-Si [18]	1302		
$CrSi_2$-Si [18]	1305		
$TiSi_2$-Si [18]	1330		
$ZrSi_2$-Si [23]	1353		
$HfSi_2$-Si [18]	1360		
Ru_2Si_3-Si [24]	1370		
VSi_2-Si [25]	1382		
$TaSi_2$-Si [18]	1385		
$ReSi_{1.75}$-Si [26]	1380		
$MoSi_2$-Si [18]	1400		
WSi_2-Si [27]	1400		

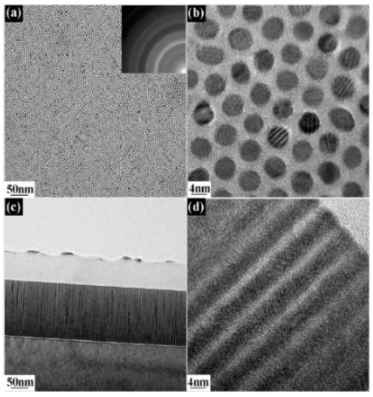


Figure 4. HRTEM images of the Pd_2Si-Si system sputtered by using deposition condition 1. a) A low-magnification image and b) high-magnification lattice image in plane view. c) A low-magnification image and d) high-magnification image in cross-sectional view.

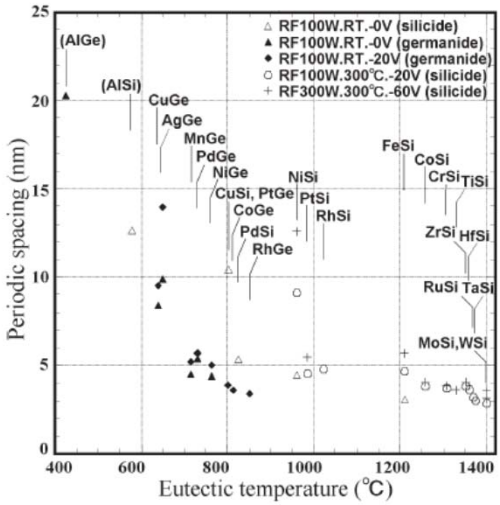


Figure 3. Plot of periodic spacing versus eutectic temperature for various phase-separated silicide and germanide systems. △ represents silicide systems deposited under condition 1; ▲ represents germanide systems deposited under condition 1; ◆ represents germanide systems deposited under condition 2; ○ represents silicide systems deposited under condition 3; + represents silicide systems deposited under condition 4.

Chem 253, UC, Berkeley

ELSEVIER

Physica C 378–381 (2002) 360–363

PHYSICA C

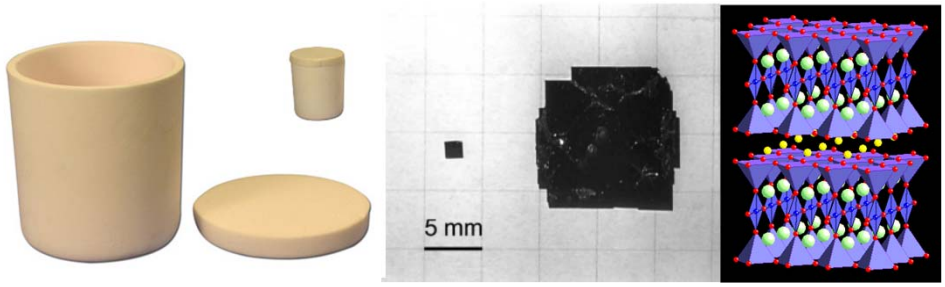
www.elsevier.com/locate/physc

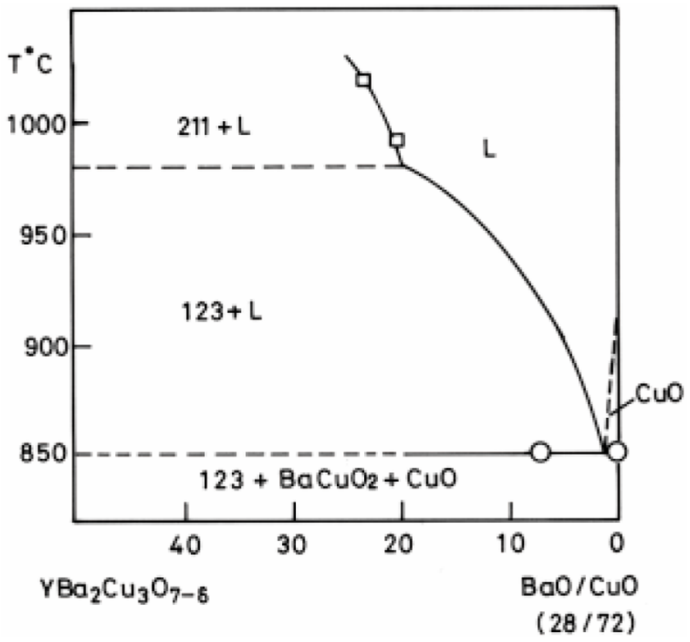
High-quality RE-123 single crystals grown in $BaZrO_3$ crucible

Y. Morita, T. Motohashi, S. Sugihara, H. Yamauchi *

Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Accepted 26 December 2001





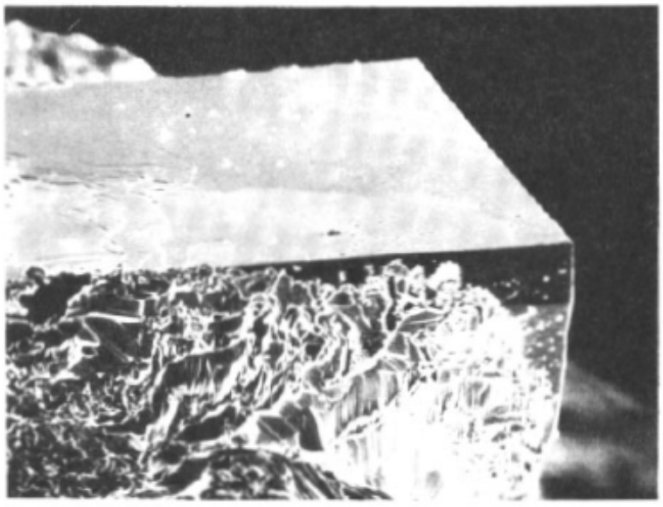
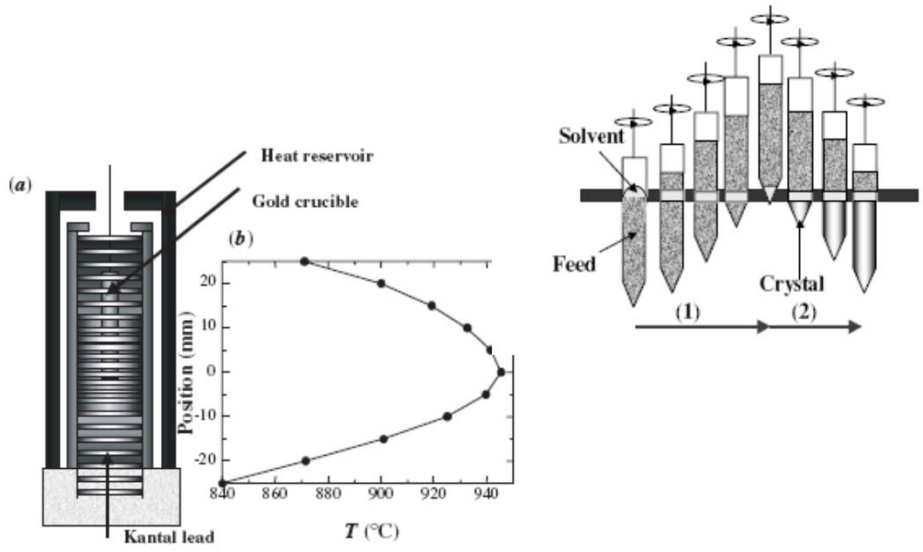
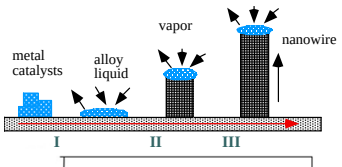


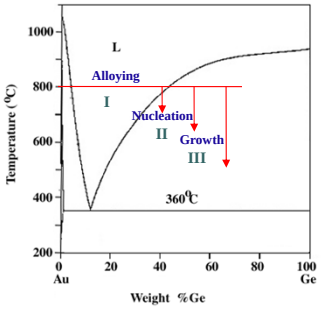
Figure 5. As-grown 123 single crystal with equilibrium-shaped habit, size 3 × 2 × 1 mm [34].



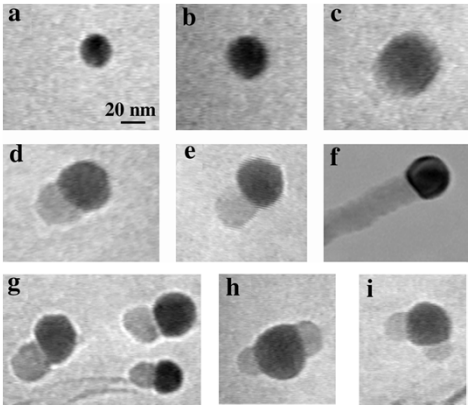
travelling solvent zone melting method

Vapor-Liquid-Solid Nanowire Growth



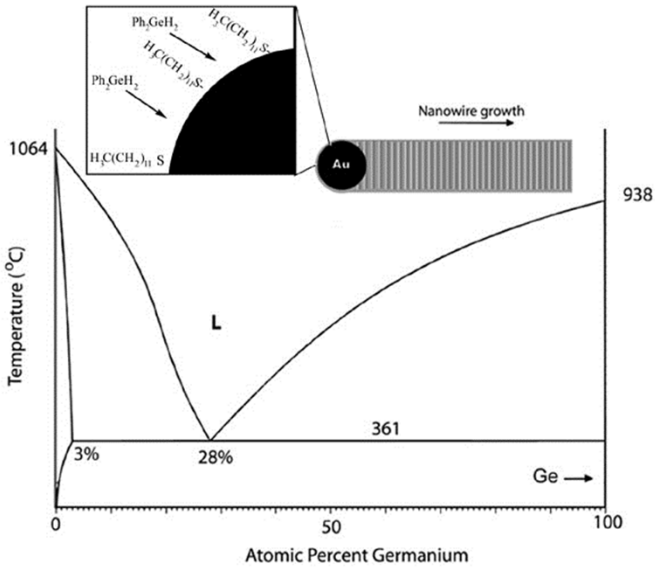


800 deg. In-situ TEM



Unidirectional growth is the consequence of an anisotropy in solid-liquid interfacial energy.

Y. Wu et al. *J. Am. Chem. Soc*. **2001**, *123*, 3165



Chem 253, UC, Berkeley

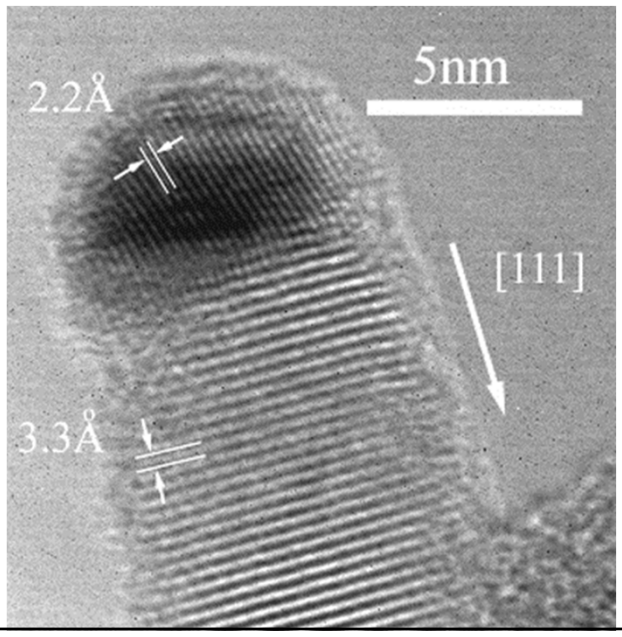
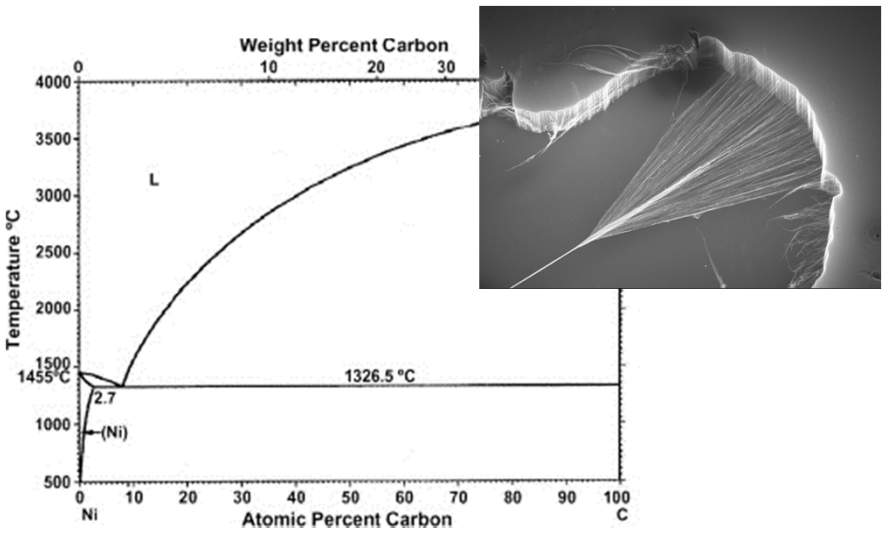


Table 1. Summary of single crystal nanowires synthesized. The growth temperatures correspond to ranges explored in these studies. The minimum and average nanowire diameters were determined from TEM and FE-SEM images. Structures were determined using electron diffraction and lattice resolved TEM imaging: ZB, zinc blende; W, wurtzite; and D, diamond structure types. Compositions were determined from EDX measurements made on individual nanowires. All of the nanowires were synthesized using Au as the catalyst, except GaAs, for which Ag and Cu were also used. The GaAs nanowires obtained with Ag and Cu catalysts have the same size distribution, structure, and composition as those obtained with the Au catalyst.

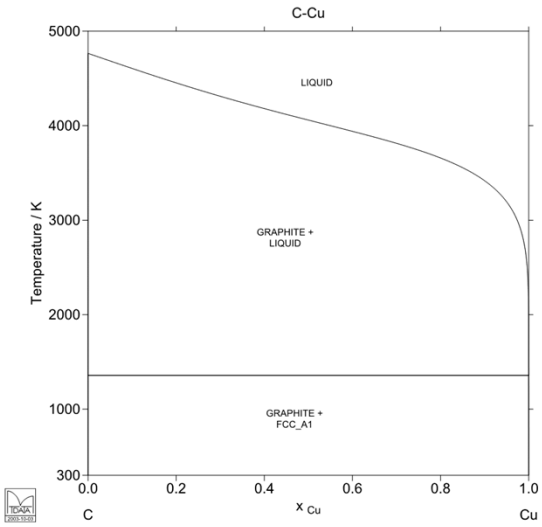
Material	Growth Temperature [°C]	Minimum Diameter [nm]	Average Diameter [nm]	Structure	Growth Direction	Ratio of Components
GaAs	800–1030	3	19	ZB	<111>	1.00 : 0.97
GaP	870–900	3–5	26	ZB	<111>	1.00 : 0.98
$GaAs_{0.6}P_{0.4}$	800–900	4	18	ZB	<111>	1.00 : 0.58 : 0.41
InP	790–830	3–5	25	ZB	<111>	1.00 : 0.98
InAs	700–800	3–5	11	ZB	<111>	1.00 : 1.19
$InAs_{0.5}P_{0.5}$	780–900	3–5	20	ZB	<111>	1.00 : 0.51 : 0.51
ZnS	990–1050	4–6	30	ZB	<111>	1.00 : 1.08
ZnSe	900–950	3–5	19	ZB	<111>	1.00 : 1.01
CdS	790–870	3–5	20	W	<100>, <002>	1.00 : 1.04
CdSe	680–1000	3–5	16	W	<110>	1.00 : 0.99
$Si_{1-x}Ge_x$	820–1150	3–5	18	D	<111>	$Si_{1-x}Ge_x$

Chem 253, UC, Berkeley

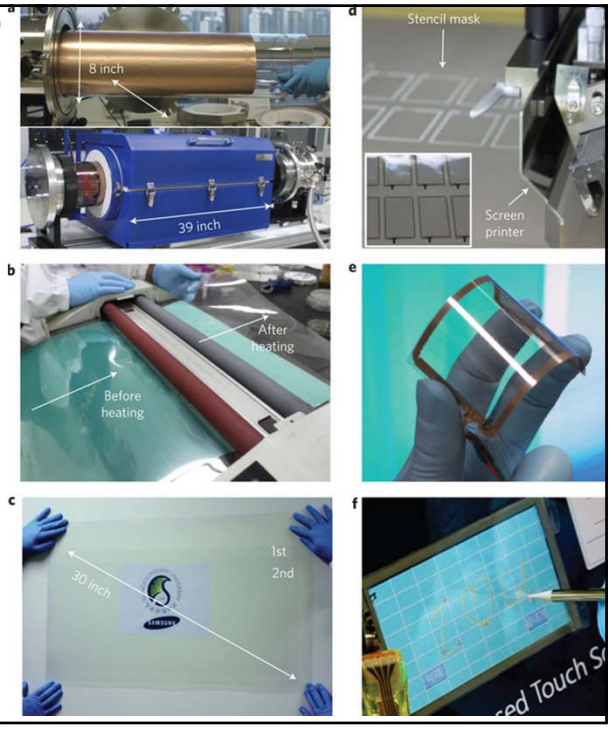
Case Study: Carbon nanotube growth



Case Study: graphene growth



Roll-to-roll production of 30-inch graphene films



Nature Nanotechnology
Volume:5,
Pages:574–578
Year published:(2010)