CONSTITUIÇÃO E DIAGRAMAS DE FASES

Professor: Gilberto Carvalho Coelho

Carga Horária: 60 horas

Bibliografia:

1 - Rhines, F. N. Phase Diagram in Metallurgy - Their Development and Application. Mcgraw-Hill, New York, 1956.

2 - Kaltenbach, K. e Gama, S. Phase Diagrams - The Maps of Materials. Apostila DEMAR, Lorena, 1983.

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8 - Massalski, T. B. Binary Alloys Phase Diagrams. ASM, Metals Park, Ohio, 1990.

9 - Callister Jr., W.D., Ciência e Engenharia de Materiais: Uma Introdução. LTC, Rio de Janeiro, 2002.

CONSTITUIÇÃO E DIAGRAMAS DE FASES

Carga horária: 60 horas

Conteúdo:

1 - Introdução
2 - Sistemas unários
3 - Sistemas binários isomorfos
4 - Sistemas binários eutéticos
5 - Sistemas binários eutetóides
6 - Sistemas binários monotéticos
7 - Transformações congruentes
8 - Sistemas binários peritéticos
9 - Sistemas binários peritetóides
10 - Sistemas binários sintéticos
11 - Diagramas de fases binários complexos
12 - Sistemas ternários isomorfos
13 - Equilíbrio ternário de três fases
14 - Equilíbrio ternário de quatro fases, Classe I
15 - Equilíbrio ternário de quatro fases, Classe II
16 - Equilíbrio ternário de quatro fases, Classe III
17 - Transformações congruentes em sistemas ternários
18 - Sistemas ternários complexos

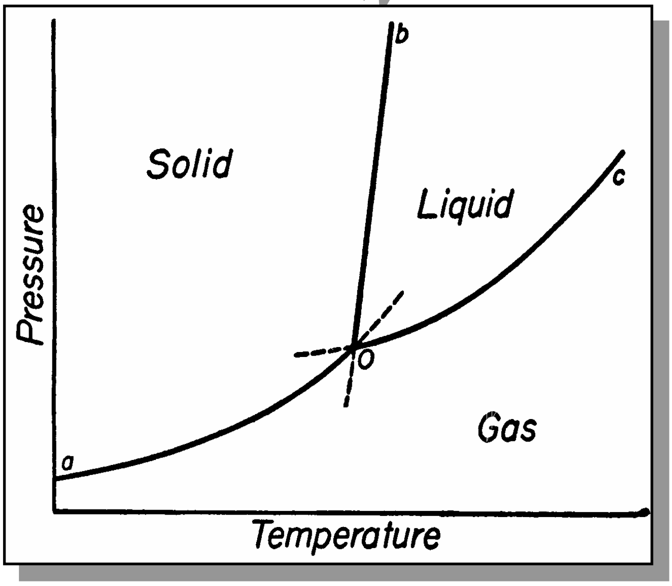
Constituição e Diagramas de Fases

DIAGRAMA

Variáveis termodinâmicas

- Pressão
- Temperatura
- Composição

FASE



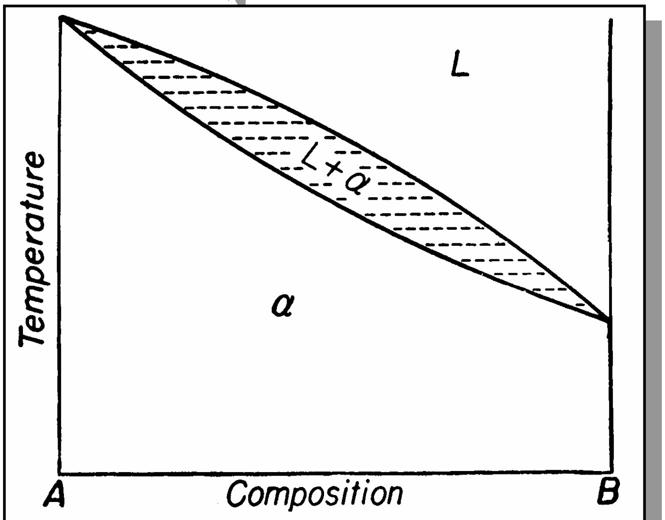


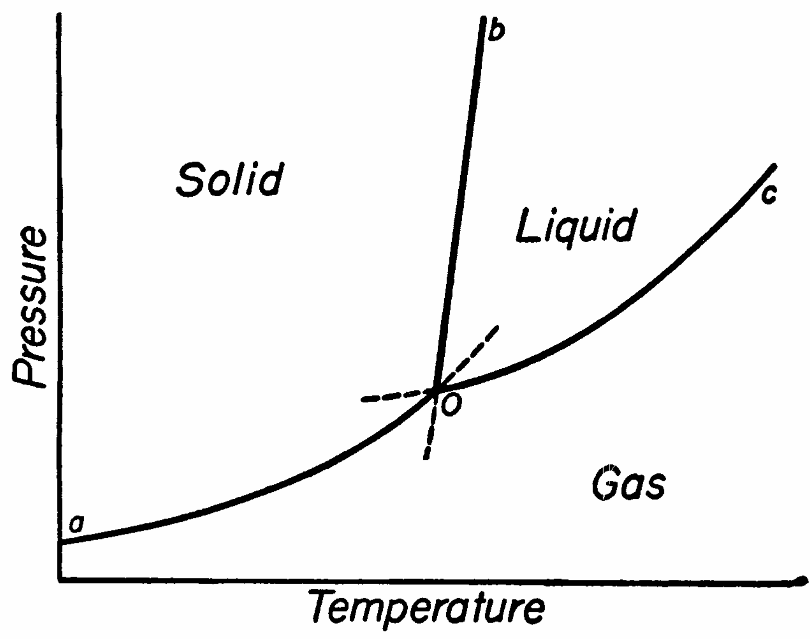
FIG. 3-5

CONSTITUIÇÃO

- Calor específico, entalpia, entropia
- Energia livre
- EQUILÍBRIO

(tempo?!? materiais na engenharia?!?)

REGRA DAS FASES



$\boxed{P + F = C + 2}$ (F = m - n)

P número de fases em equilíbrio (restrições)
F grau de liberdade
C número de <u>componentes</u> (+2 = variáveis independentes)

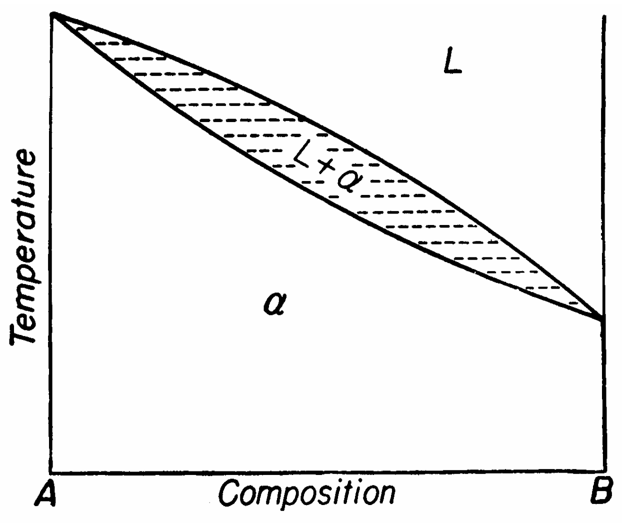
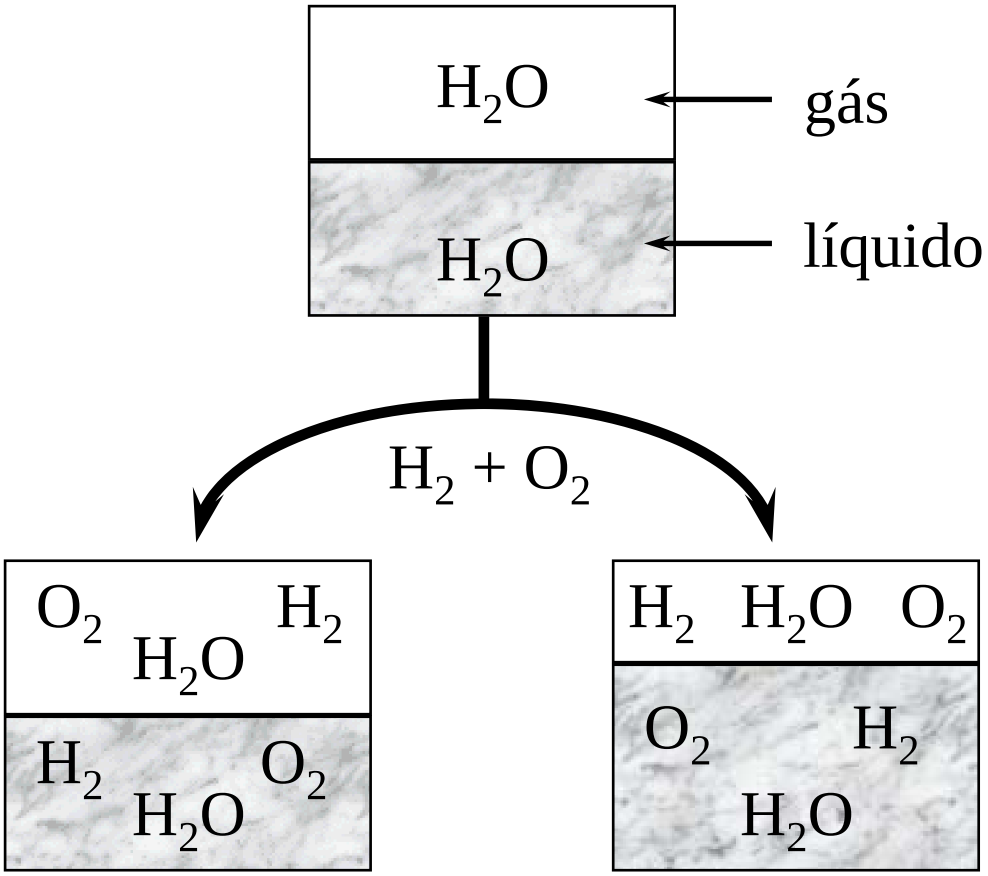


FIG. 3-5

P + F = C + 1 (P=const.)

COMPONENTE (≠ ELEMENTO?)



H_2O ← gás

H_2O ← líquido

$H_2 + O_2$

O_2 H_2 H_2O

H_2 O_2 H_2O

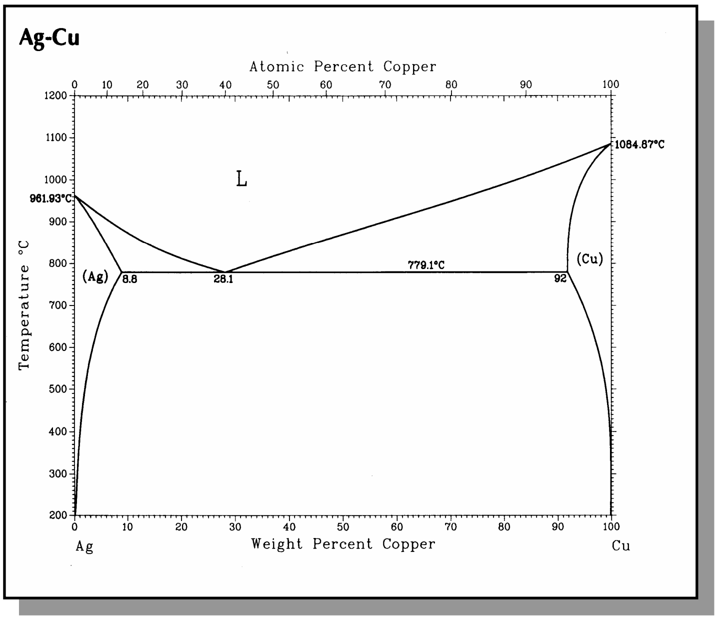
H_2 H_2O O_2

O_2 H_2 H_2O

baixa T
- 2 elementos
- 3 componentes

alta T
- 2 elementos
- 2 componentes

$H_2 + O_2 = H_2O$



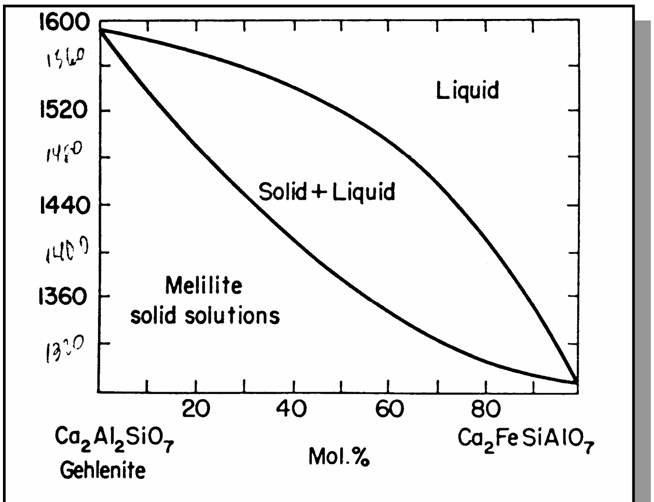


FIG. 953.—System $Ca_2Al_2SiO_7$ (gehlenite)–$Ca_2FeSiAlO_7$.

R. W. Nurse and H. G. Midgley, *J. Iron Steel Inst.* (*London*), **174**, 124 (1953).

Fase

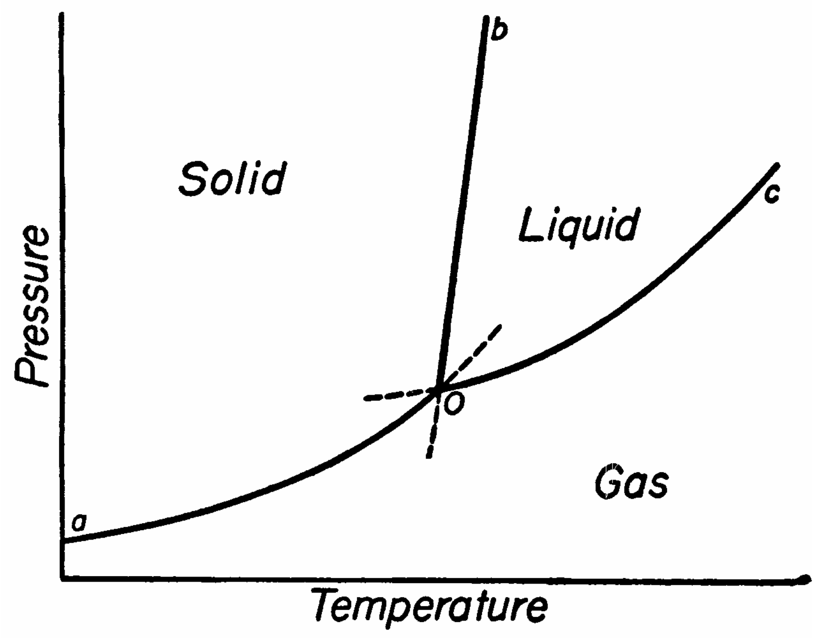
é qualquer porção homogênea de um sistema.

Diferentes porções homogêneas à mesma temperatura, pressão e composição como gotas ou grãos, são consideradas como a mesma fase.

Componente

o número de componentes de um sistema é o menor número de variáveis constituintes independentes através das quais a composição de cada fase envolvida no equilíbrio pode ser expressa.

2 - SISTEMAS UNÁRIOS



1 componente ⇨ Variáveis: *P* e *T*

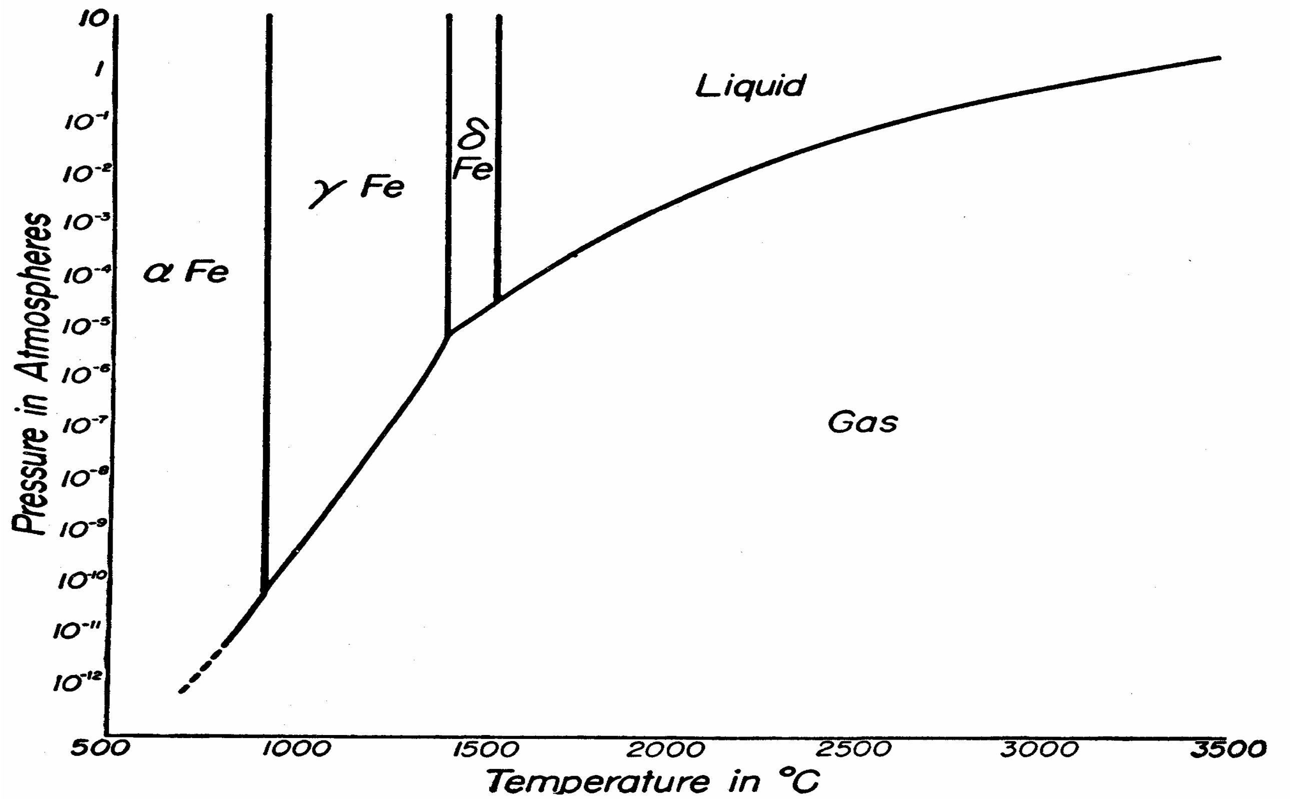


FIG. 2-4. Estimated pressure-temperature diagram of iron.

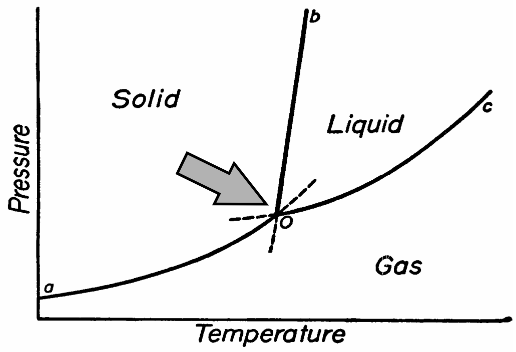
2.1 - Equilíbrio Invariante (F = 0)

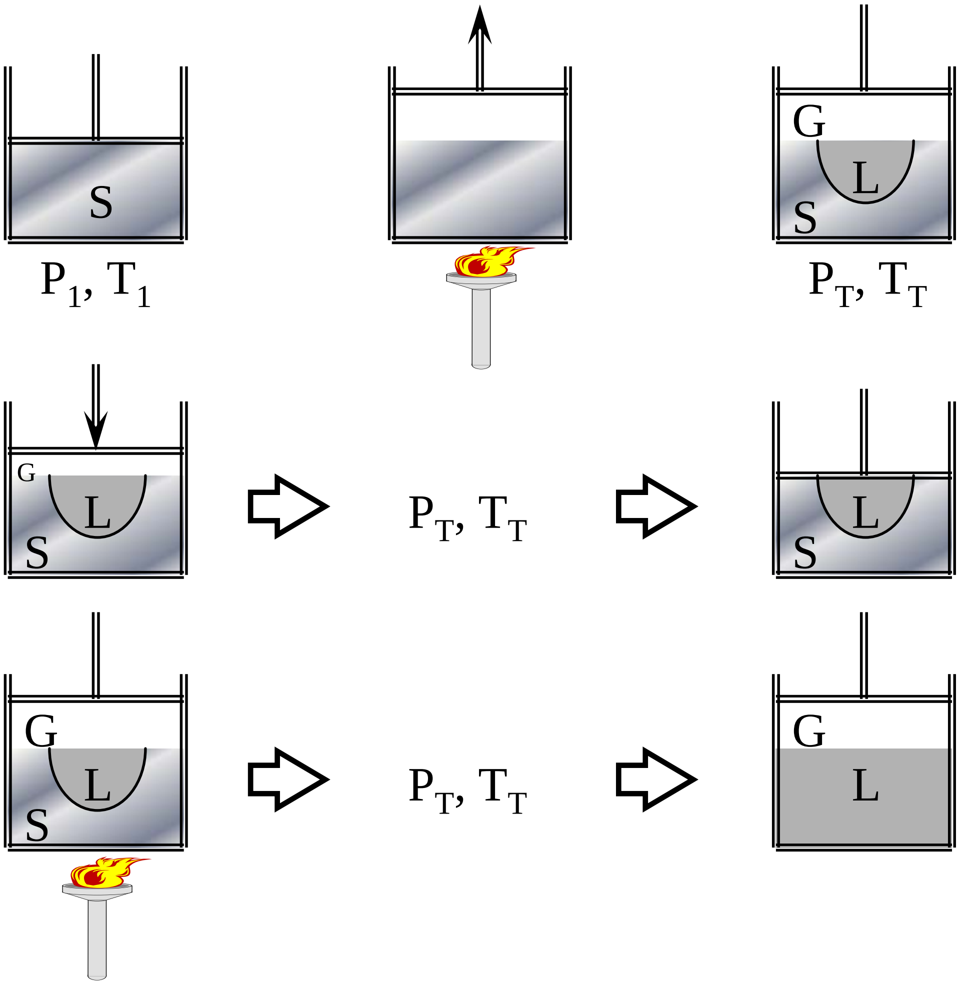
Regra das fases

$$F = 0 \quad \text{e} \quad C = 1$$

$$P + 0 = 1 + 2$$

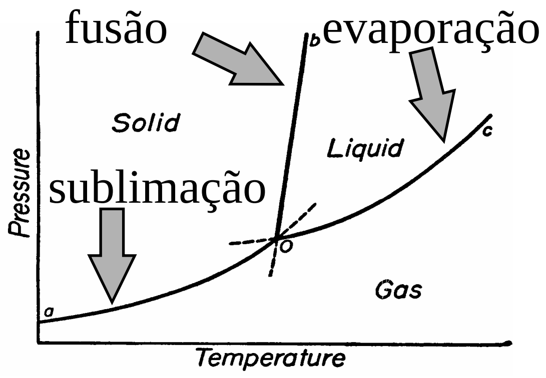
$$\boxed{P = 3}$$





Geral: a regra das fases não está relacionada com as quantidades das fases presentes ou com suas propriedades, mas somente com o número de fases presentes no equilíbrio e com suas composições, temperatura e pressão.

2.2 - Equilíbrio Univariante (F = 1)



Regra das fases

$$F = 1 \quad \text{e} \quad C = 1$$

$$P + 1 = 1 + 2$$

$$\boxed{P = 2}$$

Formas das curvas

Le Chatelier (qualitativo)

Quando uma ação é exercida sobre o sistema, este varia de forma a anular os efeitos desta ação.

Clausius-Clapeyron (quantitativo)

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{tr}}}{T\,\Delta V_{\mathrm{tr}}}$$

Equilíbrio univariante metaestável

Exemplo: subresfriamento do equilíbrio L+G

A extensão de uma curva de equilíbrio bifásico para além do equilíbrio trifásico que a limita ocorre para dentro do campo de estabilidade da terceira fase não presente no equilíbrio bifásico.

TABLE 12-1. VAPOR PRESSURE OF THE ELEMENTS*

(Temperature in degrees Kelvin for various partial pressures in atmospheres)

Species	10^{-6} atm	10^{-5} atm	10^{-4} atm	10^{-3} atm	10^{-2} atm	1 atm
A						87.3(l)
Ag	1200(s)	1305	1442	1607	1816	2485
Al	1290(l)	1405	1545	1725	1940	2600
As_4	477(s)	517	563	622	708	895
At_2	......	270(s)	320	350	390	500
Au	1570(l)	1720	1896	2112	2388	3239
B	1500(s)	1600	1750	1900	2150	2800(l)
Ba	810(s)	890	985(l)	1116	1293	1911
Be	1390(s)	1505	1655(l)	1830	2070	2780
Bi	873(l)	960	1060	1190	1360	1900
Br_2	173(s)	186	203	222	245	331(l)
C	2720(s)	2920	3170	3450	3800	4775
Ca	790(s)	867	961	1075	1231(l)	1755
Cb	2820(l)	3050	3340	3700	4120	5400
Cd	485(s)	530	585(l)	657	744	1038
Ce	1450(l)	1550	1700	1850	2100	2800
Cl_2	114(s)	123	139	153	169	239(l)
Co	1750(s)	1900(l)	2100	2300	2600	3370
Cr	1350(s)	1465	1600	1755	1960	2495(l)
Cs	383(l)	425	476	544	634	963
Cu	1400(l)	1530	1685	1875	2117	2868
F_2	......	......	......	......	58(l)	85
Fr(87)	......	......	490(l)	......	......	950
Fe	1550(s)	1680	1837(l)	2033	2277	3008
Ga	1225(l)	1350	1500	1690	1920	2700
Ge	1370(l)	1500	1670	1880	2150	2980
H_2	......	......	......	......	......	20.39(l)
He	......	......	......	......	......	4.22(l)
Hf	2850(l)	3100	3350	3750	4150	5500
Hg	287(l)	316	351	394	449	634
I_2	241(s)	260	282	308	341	456(l)
In	1100(l)	1210	1350	1510	1730	2440
Ir	2580(s)	2800(l)	3040	3350	3700	4800
K	429(l)	475	534	605	702	1052
Kr	......	......	......	......	......	119.9(l)
La	1500(l)	1650	1800	2000	2250	3000
Li	705(l)	775	865	980	1130	1640
Mg	653(s)	715	789	881	1000(l)	1399
Mn	1140(s)	1240	1360	1570(l)	1750	2370
Mo	2530(s)	2740	3000(l)	3330	3750	5077
N_2	......	......	......	......	......	77.4(l)
Na	510(l)	558	623	705	813	1187
Ne	......	......	......	......	......	27.3(l)
Ni	1630(s)	1765(l)	1930	2130	2380	3110

TABLE 12-1. VAPOR PRESSURE OF THE ELEMENTS.*—(*Continued*)

Species	10^{-6} atm	10^{-5} atm	10^{-4} atm	10^{-3} atm	10^{-2} atm	1 atm
O_2	......	......	......	......	......	90.2(l)
Os	2700(s)	2900	3160(l)	3470	3850	4900
P_4(yellow)	244(s)	268	296	334(l)	382	553
Pa	2250(l)	2450	2700	2950	3300	4500
Pb	887(l)	975	1088	1226	1408	2010
Pd	1660(s)	1800	2000(l)	2240	2530	3440
Po_2	......	660(s)	750	835(l)	945	1300
Pt	2160(l)	2340	2550	2820	3140	4100
Ra	650(s)	700	770	850	965	1410(l)
Rb	403(l)	445	496	561	650	952
Re	2900(s)	3150	3450(l)	3850	4300	5800
Rh	2200(s)	2400(l)	2600	2850	3200	4150
Rn	......	......	......	......	......	211(l)
Ru	2480(s)	2670	2900(l)	3180	3500	4500
S_2	......	......	500(l)			
Sb_2	860(s)	940(l)	1025	1160	1340	1890
Sc	1540(s)	1680(l)	1850	2050	2300	3000
Se_2	525(l)	568	620	679	755	1000
		(2 atm Se_6 and 10^{-4} atm Se at 1000°K)				
Si	1480(s)	1600	1740(l)	1920	2140	2750
Sn	1300(l)	1450	1600	1850	2150	3000
Sr	740(s)	810	900	1010	1150(l)	1657
Ta	3300(l)	3600	3900	4300	4800	6300
Tc(43)	2550(l)	2750	3000	3300	3700	5000
Te_2	655(s)	700	758(l)	825	907	1130
Th	2250(l)	2450	2700	2950	3300	4500
Ti	1640(s)	1800	1990	2210(l)	2500	3400
Tl	795(l)	870	965	1082	1235	1730
U	2000(l)	2150	2350	2580	2900	3800
V	1970(l)	2140	2340	2550	2900	3800
W	3230(s)	3490	3780(l)	4150	4625	5950
Xe	......	......	......	......	......	165.1(l)
Y	1750(s)	1900(l)	2100	2300	2700	3500
Zn	560(s)	610	672	750(l)	852	1180
Zr	2070(s)	2250	2450(l)	2700	3000	3850

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* Taken from Leo Brewer, Report for the Manhattan Project, MDDC-438C, 1946.

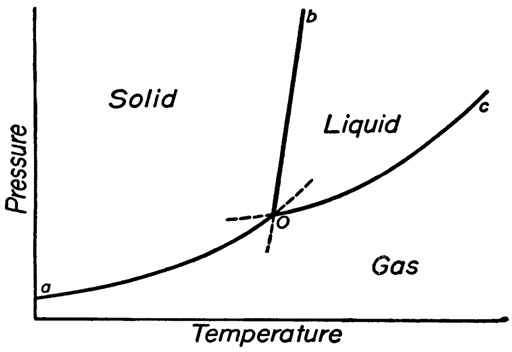
2.3 - Equilíbrio Bivariante (F = 2)

Regra das fases

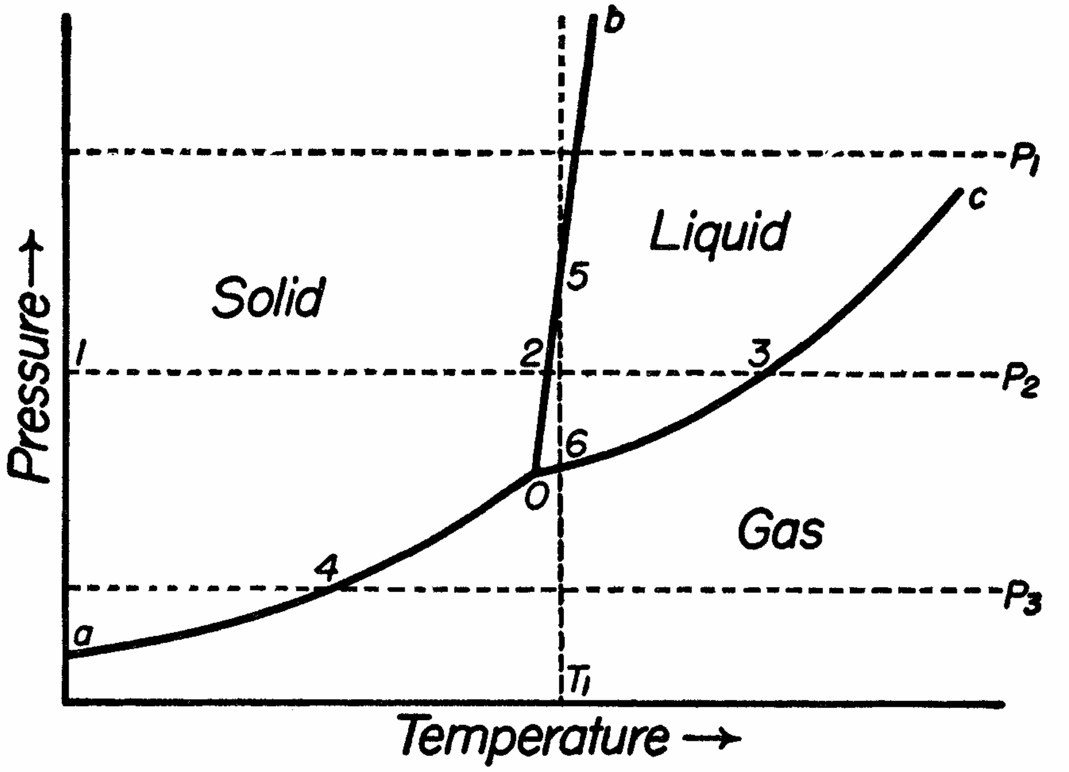
$F = 2$ e $C = 1$

$P + 2 = 1 + 2$

$\boxed{P = 1}$



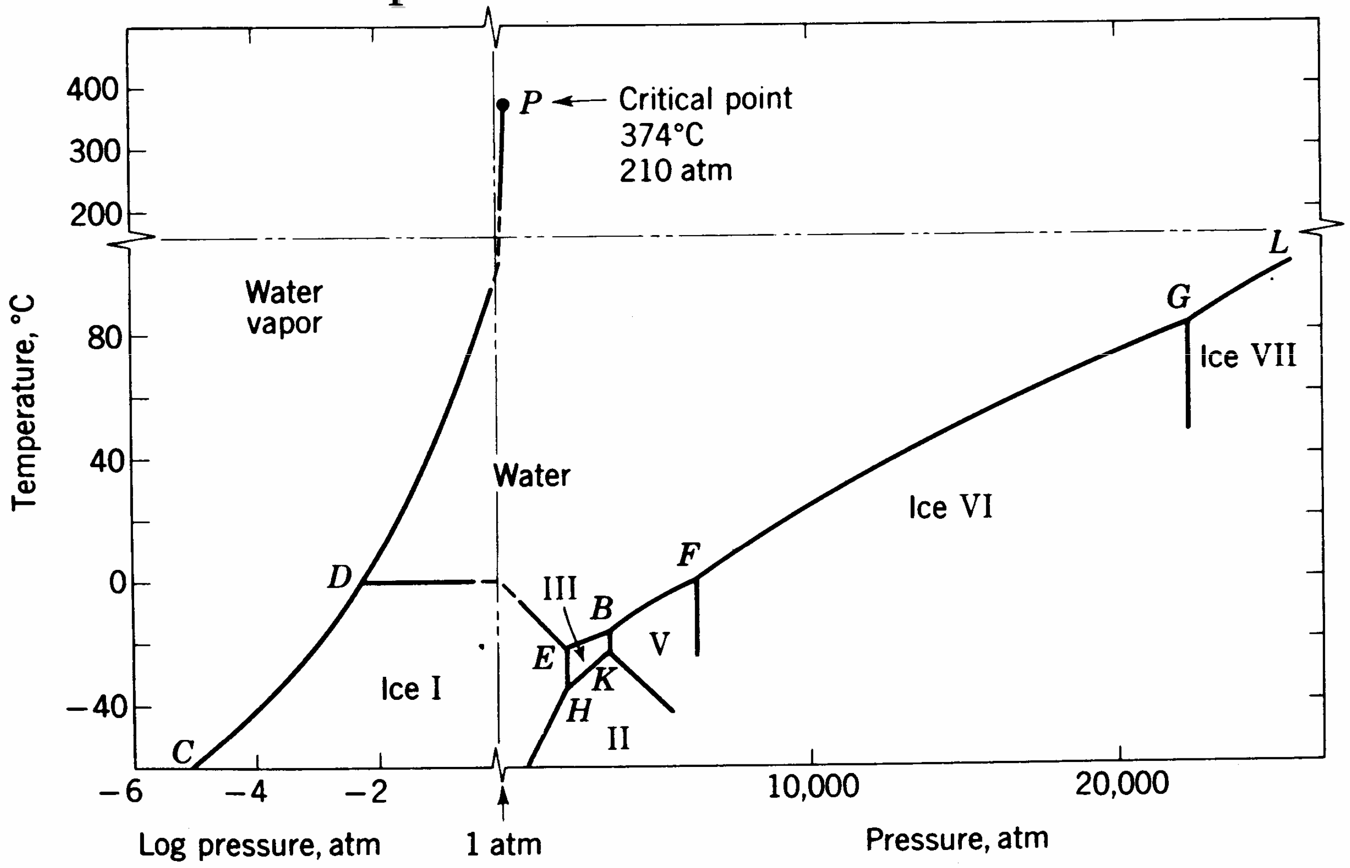
2.4 - Interpretação de diagramas unários



Metal	As	Ba	Ca	Cu	Fe	Pb
T (^{o}C)	**814**	**704**	**850**	**1083**	**1535**	**327**
P (atm)	**36**	**1.10^{-3}**	**1.10^{-4}**	**8.10^{-7}**	**5.10^{-5}**	**1.10^{-7}**

Metal	Mn	Hg	Ni	Pt	Ag	Zn
T (^{o}C)	**1240**	**-38,87**	**1455**	**1773**	**960**	**419**
P (atm)	**1.10^{-3}**	**1.10^{-9}**	**1.10^{-4}**	**1.10^{-6}**	**1.10^{-4}**	**5.10^{-2}**

2.5 - Alotropia



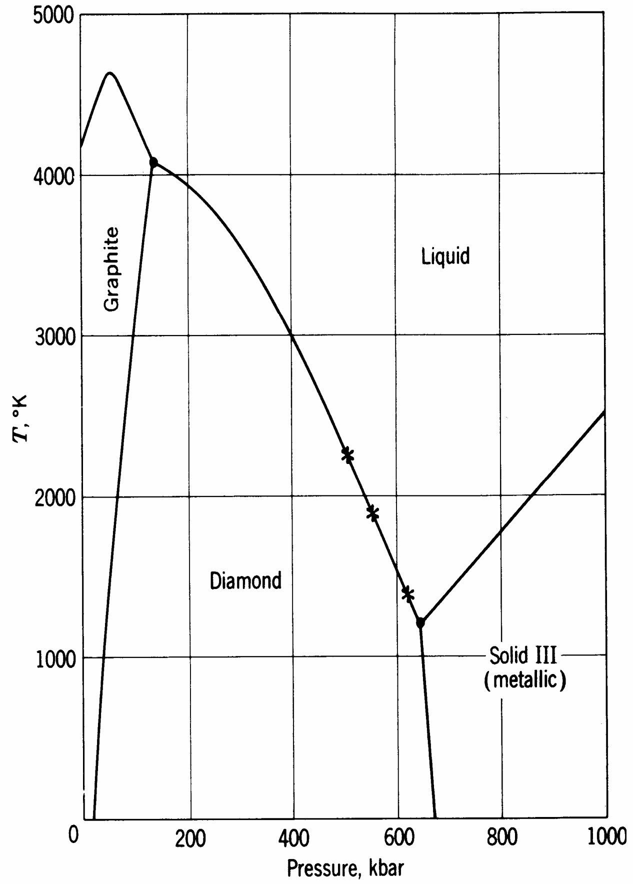


Fig. 3.11 *The carbon equilibrium T-P diagram. (From Suits.*$^{3.6}$*)*

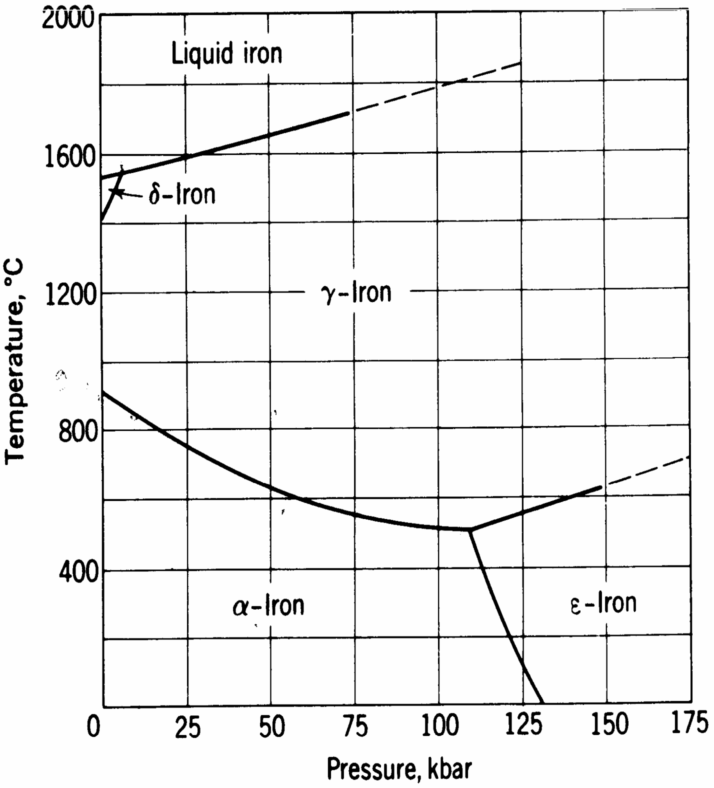


Fig. 3.5 *The iron T-P equilibrium phase diagram. (From Takahashi and Bassett, The Composition of the Earth's Interior. Copyright © 1965 by Scientific American, Inc. All rights reserved.)*

3 - SISTEMAS BINÁRIOS ISOMORFOS

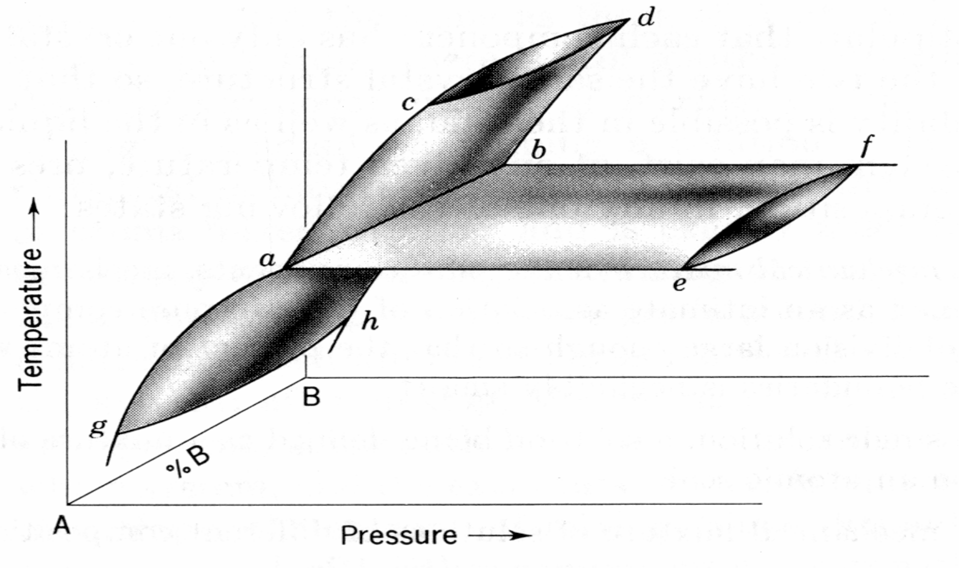


Fig. 4.1 *Schematic temperature-pressure-composition diagram for a simple two-component system at low pressures.*

Os dois componentes são mutuamente solúveis em todas as proporções e em todos os estados.

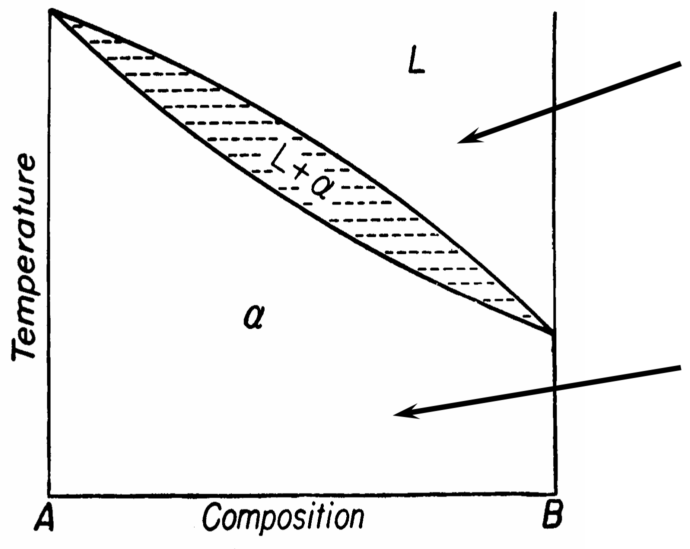


FIG. 3-5

solução líquida

solução sólida:

- substitucional
- intersticial

3.1 - O diagrama de fases

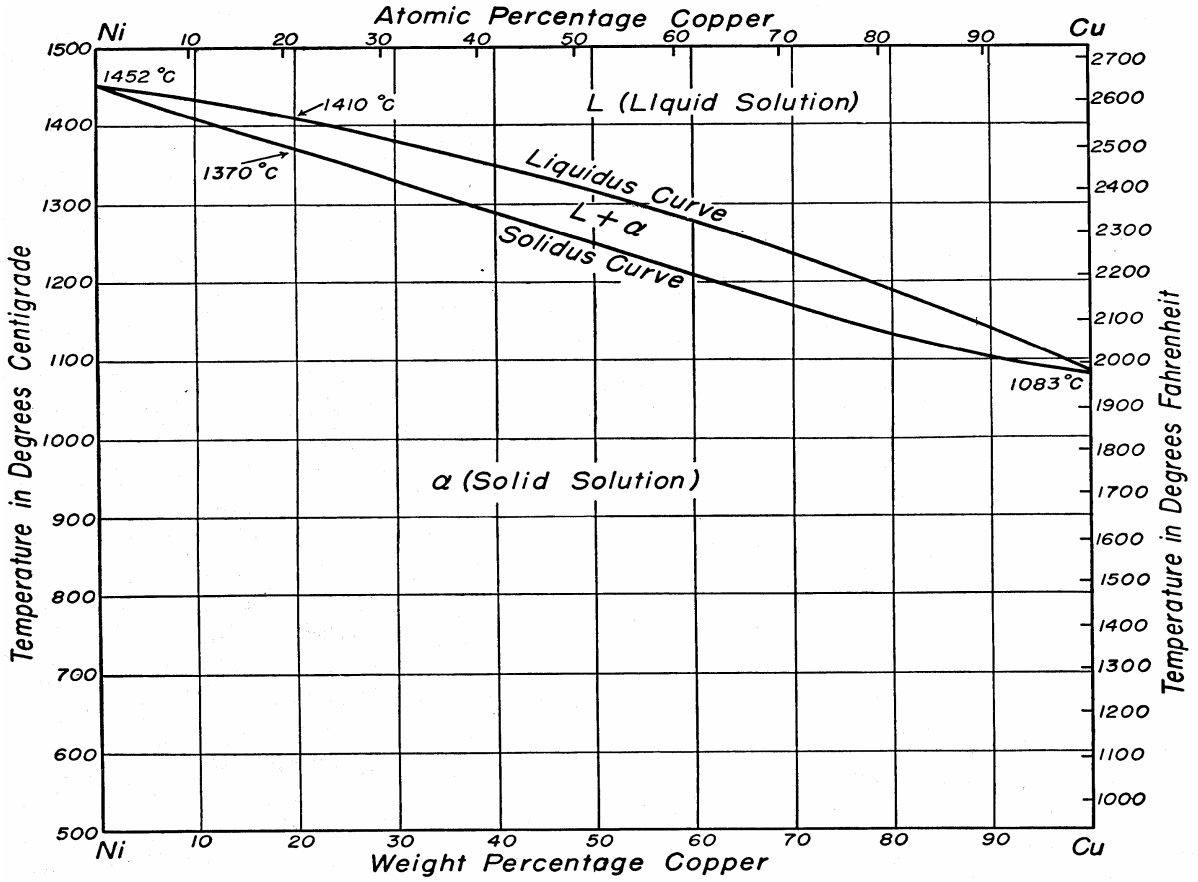


FIG. 1-1. The nickel-copper phase diagram.

Escalas de Temperatura:

- Celsius ou Kelvin (mais comuns)
- Fahrenheit

Conversão entre escalas de Composição:

- percentagem em peso para percentagem atômica

$$at.\%X = \frac{(wt.\%X)/(\text{peso at. } X)}{(wt.\%X)/(\text{peso at. } X) + (wt.\%Y)/(\text{peso at. } Y)}$$

- percentagem atômica para percentagem em peso

$$wt.\%X = \frac{(at.\%X)\ (\text{peso at. } X)}{(at.\%X)\ (\text{peso at. } X) + (at.\%Y)\ (\text{peso at. } Y)}$$

3.2 - Aplicação da regra das fases

$P + F = C + \mathbf{1}$
(*pressão constante*)

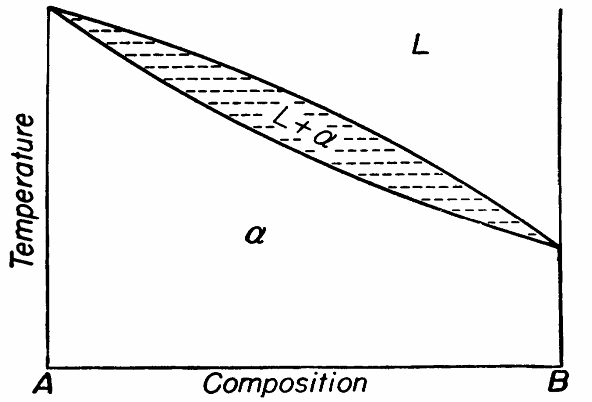


FIG. 3-5

- equilíbrio invariante:
  $F = 0$; $C = 2$; $\boldsymbol{P = 3}$
  (não existente pois só existem duas fases neste sistema em equilíbrio na pressão do diagrama)

- equilíbrio univariante:
  $F = 1$; $C = 2$; $\boldsymbol{P = 2}$
  (dado pela região hachurada L+α)

- equilíbrio bivariante:
  $F = 2$; $C = 2$; $\boldsymbol{P = 1}$
  (dados pelas regiões marcadas como **α** e **L**)

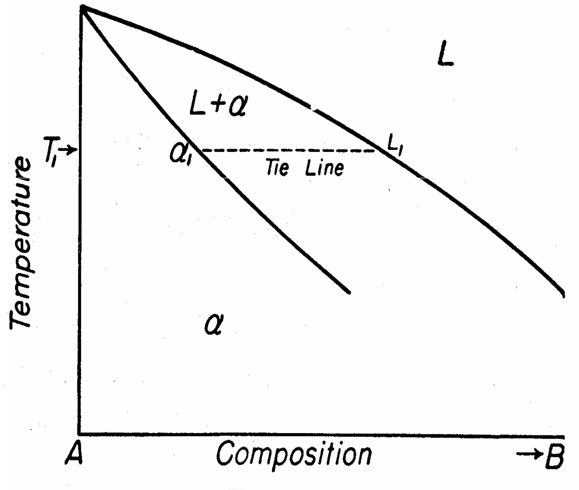


FIG. 3-3

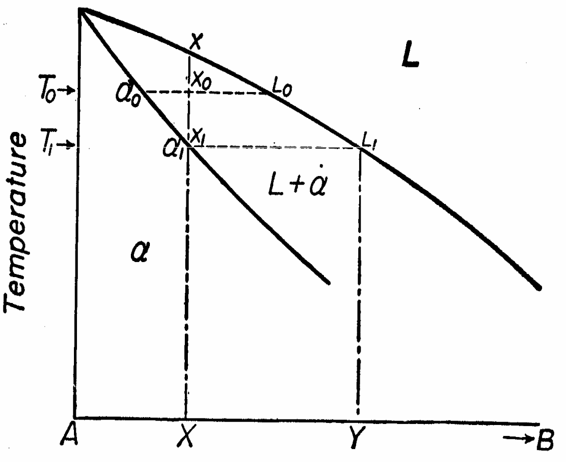


FIG. 3-4

3.3 - A regra da alavanca

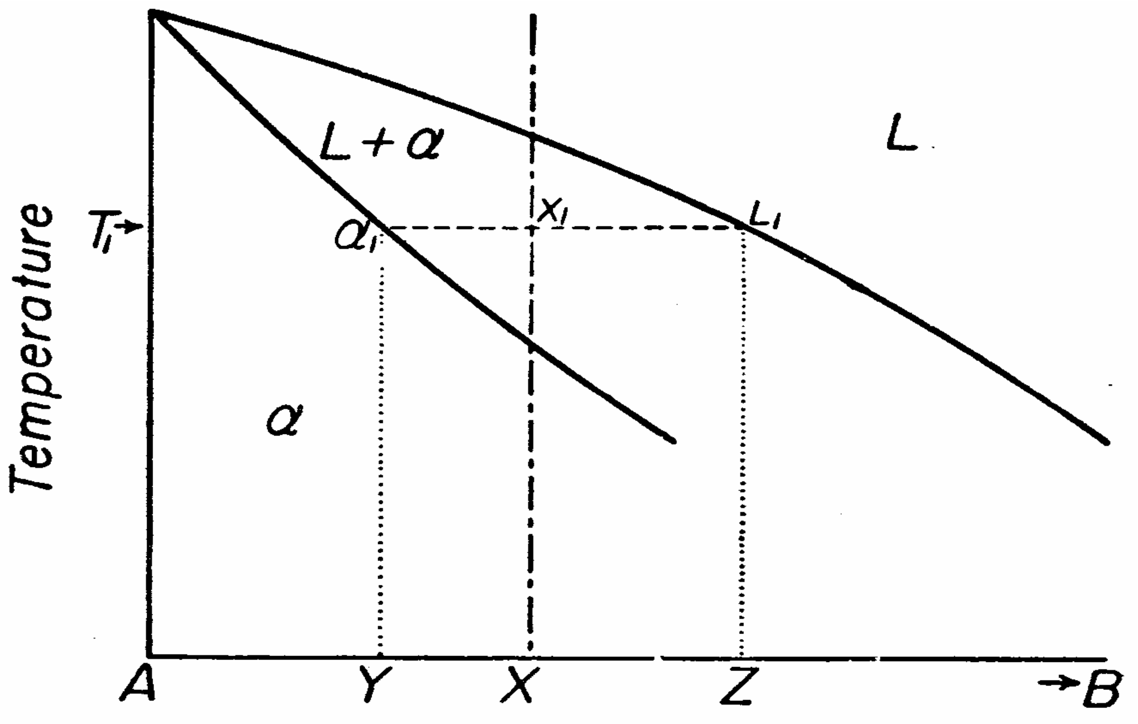


FIG. 3-6

Uma liga de composição global *X* apresenta na temperatura T_1 duas fases em equilíbrio (α e L), cujas composições são dadas pelos pontos de interseção do conódio com as curvas *solidus* e *liquidus*, α_1 e L_1 respectivamente. As quantidades das fases presentes neste equilíbrio são determinadas com o auxílio da ***Regra da Alavanca***.

quantidade de α_1:

$$\boxed{\%\alpha_1 = \frac{x_1L_1}{\alpha_1L_1} \times 100}$$

quantidade de L_1:

$$\boxed{\%L_1 = \frac{\alpha_1x_1}{\alpha_1L_1} \times 100}$$

3.4 - Solidificação em equilíbrio

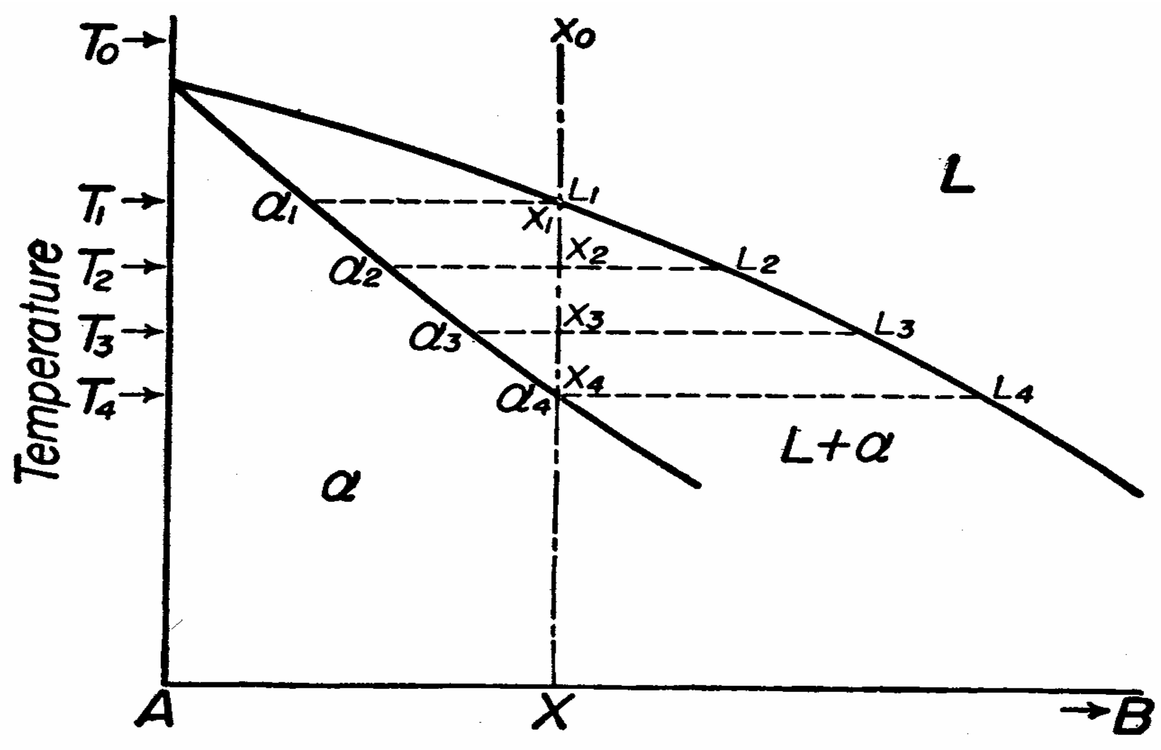


FIG. 3-7

T_1	$\%\alpha_1 = \frac{x_1L_1}{\alpha_1L_1} \times 100$	$\%L_1 = \frac{\alpha_1x_1}{\alpha_1L_1} \times 100$
T_2	$\%\alpha_2 = \frac{x_2L_2}{\alpha_2L_2} \times 100$	$\%L_2 = \frac{\alpha_2x_2}{\alpha_2L_2} \times 100$
T_3	$\%\alpha_3 = \frac{x_3L_3}{\alpha_3L_3} \times 100$	$\%L_3 = \frac{\alpha_3x_3}{\alpha_3L_3} \times 100$
T_4	$\%\alpha_4 = \frac{x_4L_4}{\alpha_4L_4} \times 100$	$\%L_4 = \frac{\alpha_4x_4}{\alpha_4L_4} \times 100$

3.5 - Solidificação fora de equilíbrio

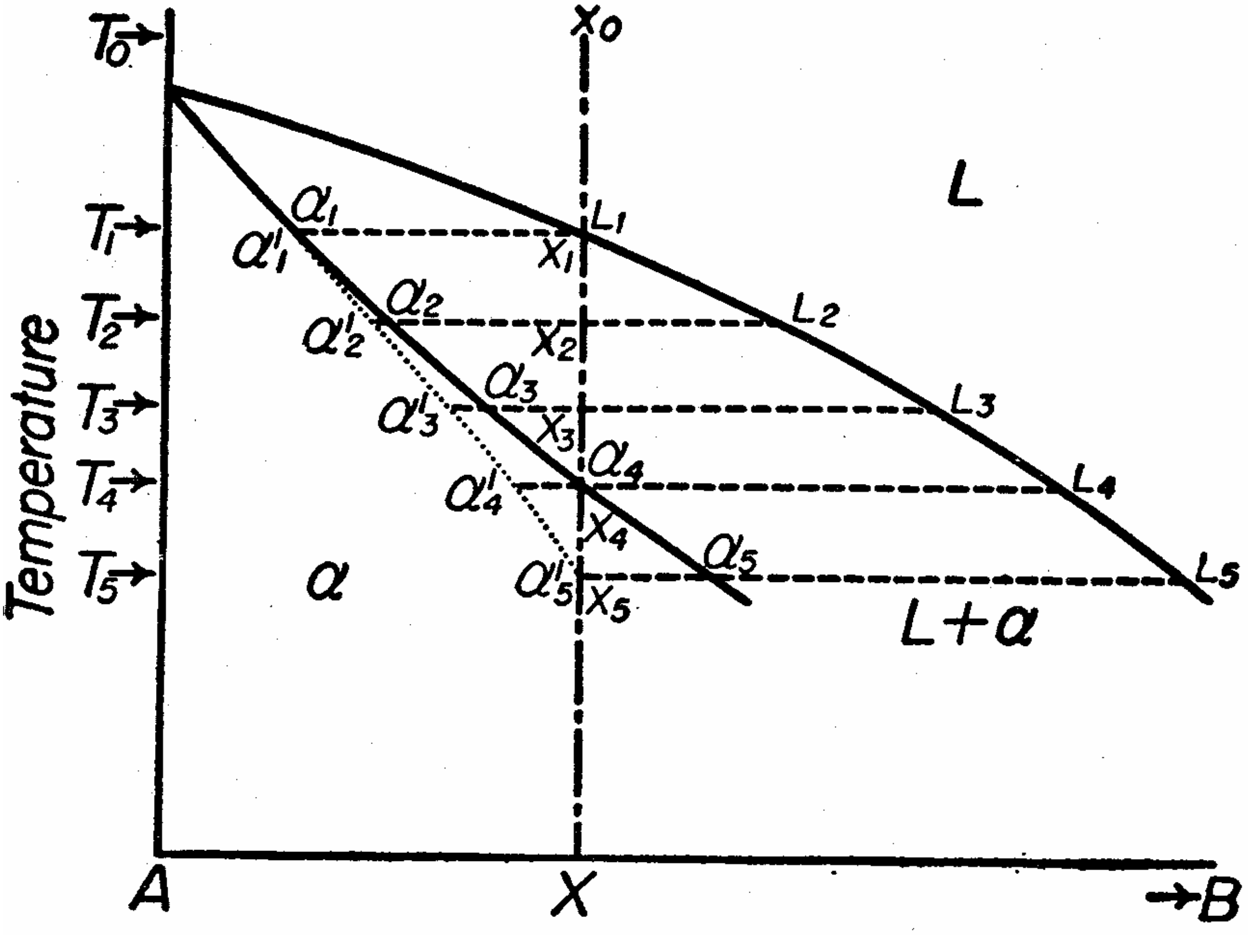
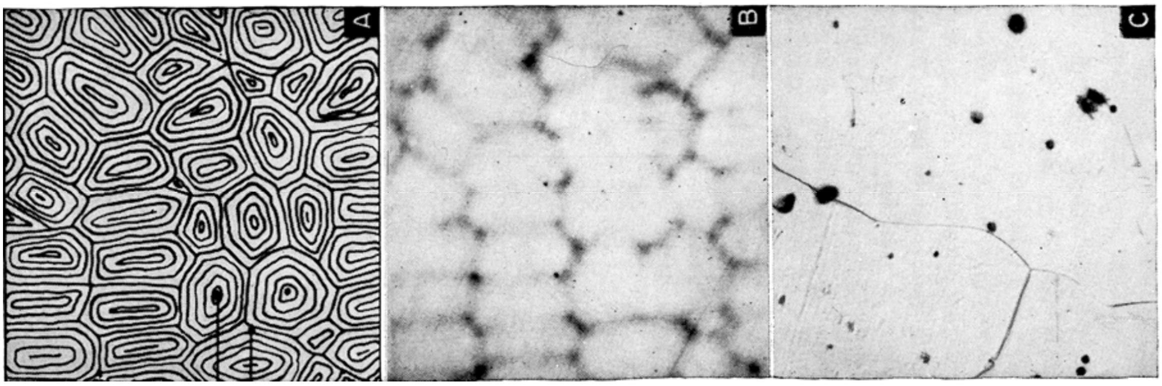


FIG. 3-8



Sistema Cu-Ni
(70wt.%Ni+30wt.%Cu)

3.6 - Mínimos e máximos

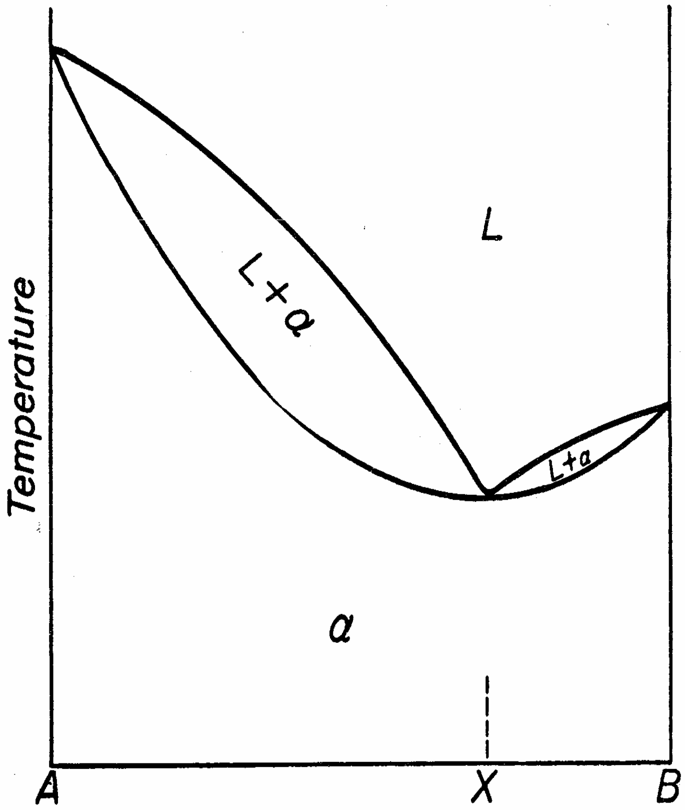


FIG. 3-13

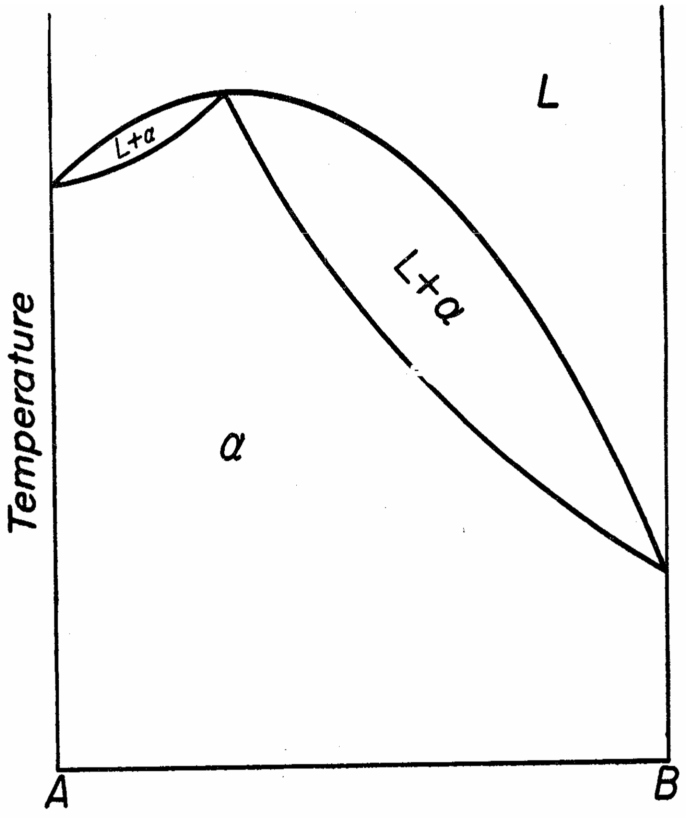
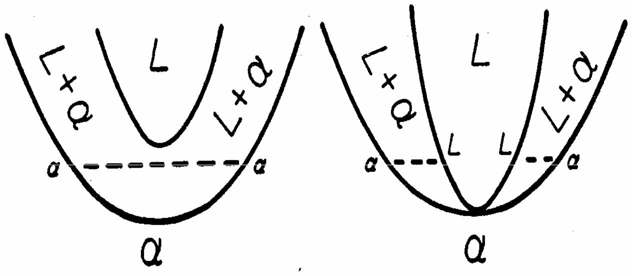


FIG. 3-15



a *b*

FIG. 3-14

3.7 - Exemplos

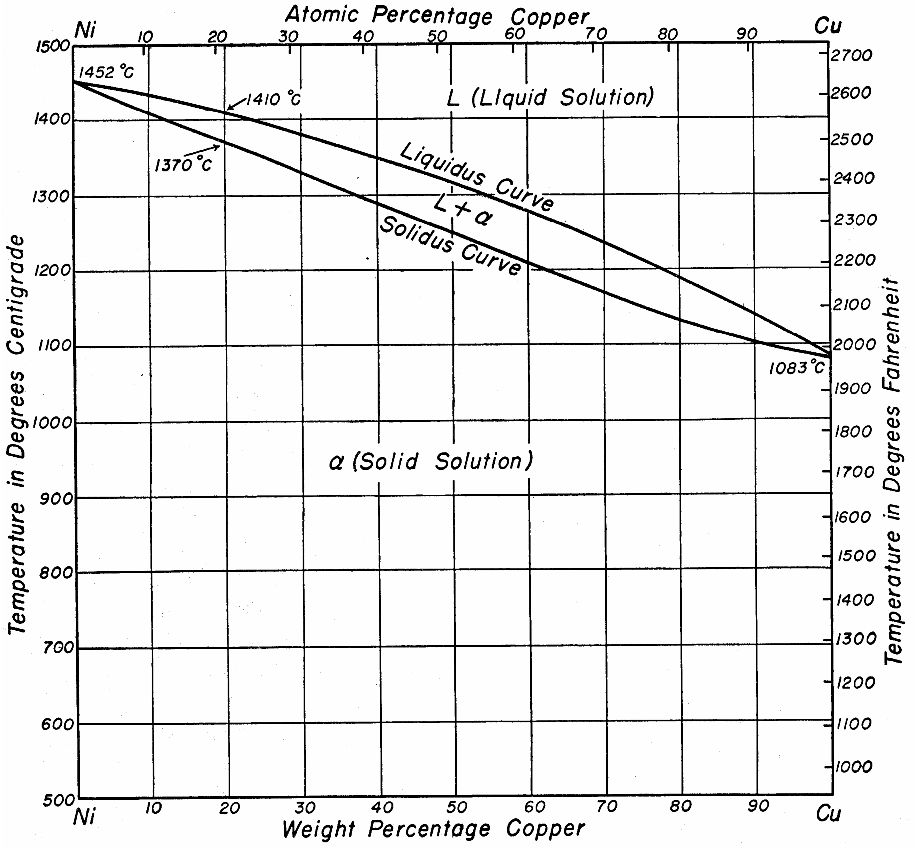


Fig. 1-1. The nickel-copper phase diagram.

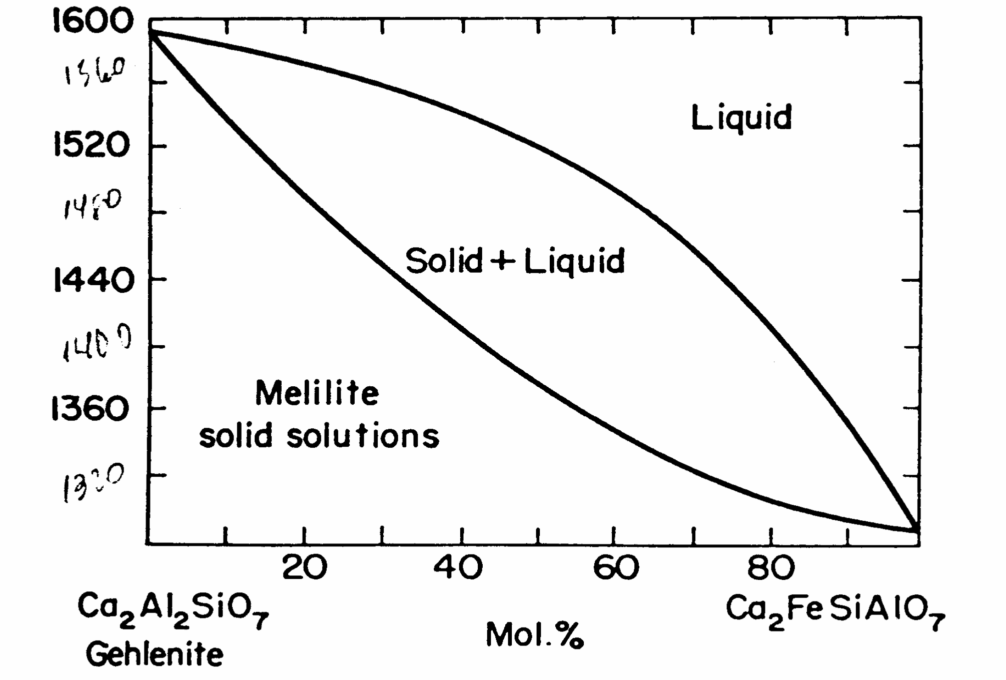


Fig. 953.—System $Ca_2Al_2SiO_7$ (gehlenite)–$Ca_2FeSiAlO_7$.

R. W. Nurse and H. G. Midgley, *J. Iron Steel Inst. (London)*, 174, 124 (1953).

4 - SISTEMAS EUTÉTICOS BINÁRIOS

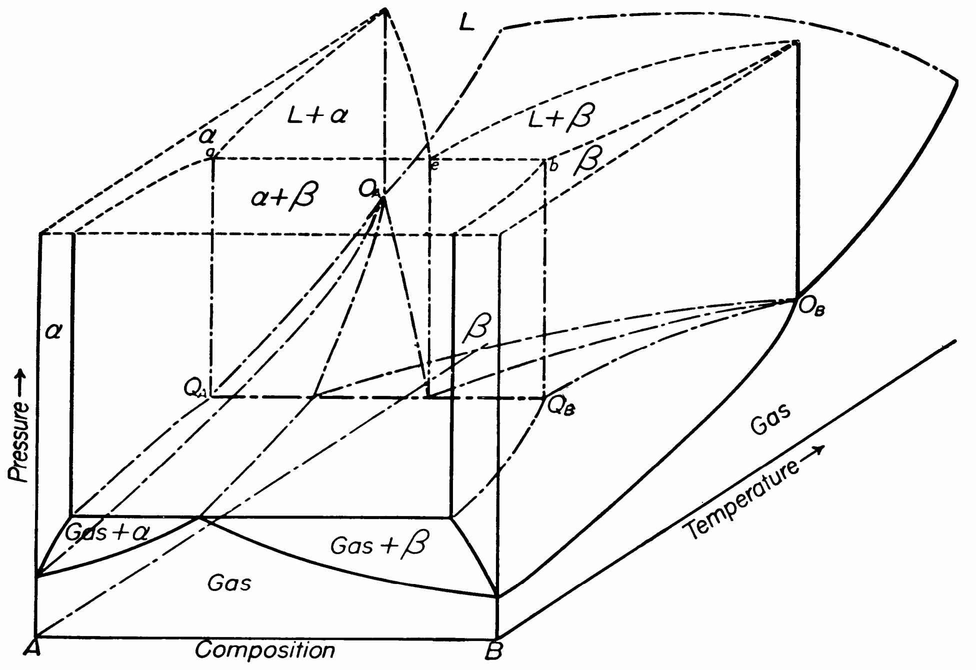


Fig. 4-2

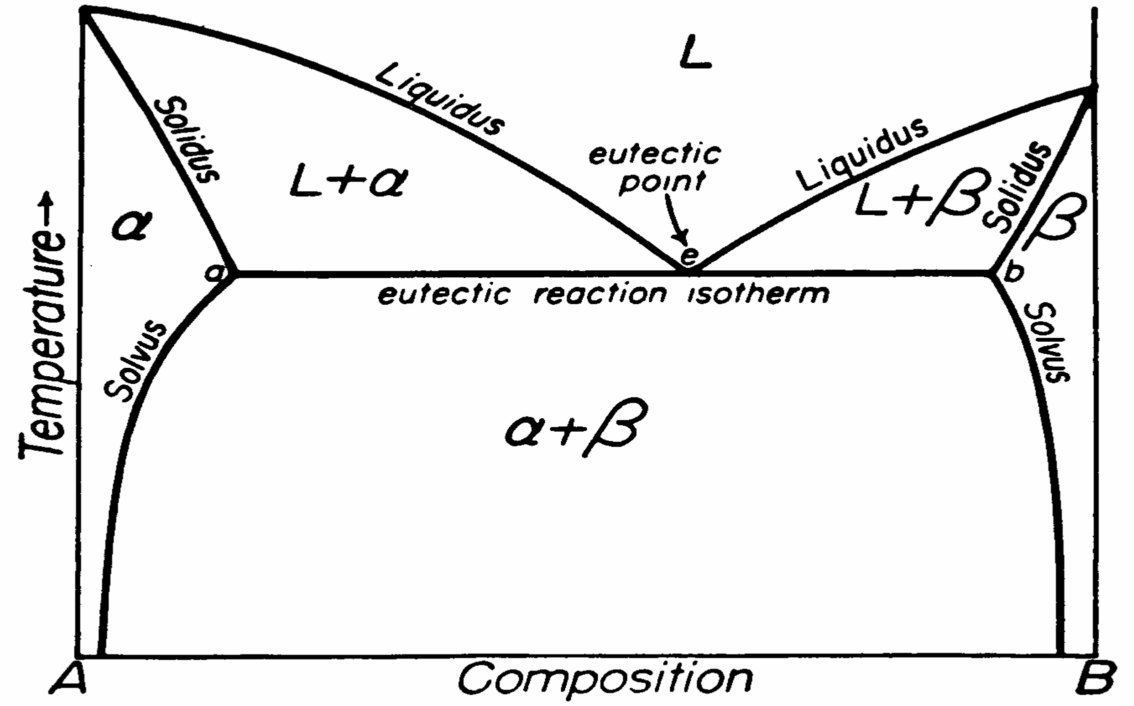


Fig. 4-1

$$L \underset{\text{aquecimento}}{\overset{\text{resfriamento}}{\rightleftarrows}} \alpha + \beta$$

4.1 - Aplicação da regra das fases

$P + F = C + \mathbf{1}$
(*pressão constante*)

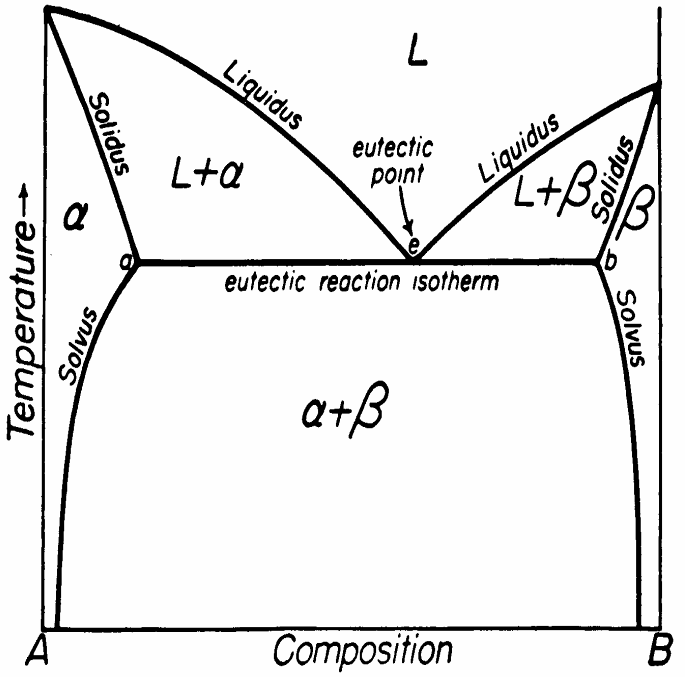


FIG. 4-1

- <u>equilíbrio invariante</u>:
  $F = 0$; $C = 2$; $\boldsymbol{P = 3}$
  (dado pela linha eutética “**a-e-b**”)

- <u>equilíbrio univariante</u>:
  $F = 1$; $C = 2$; $\boldsymbol{P = 2}$
  (regiões **L+α**, **L+β** e α+β)

- <u>equilíbrio bivariante</u>:
  $F = 2$; $C = 2$; $\boldsymbol{P = 1}$
  (regiões marcadas como α, β e **L**)

4.2 - Regra dos limites de regiões de equilíbrio

Qualquer região de ***P*** fases em equilíbrio só pode ser limitada por regiões de ***P* ☝ *1*** fases.

4.3 - Liga de composição eutética

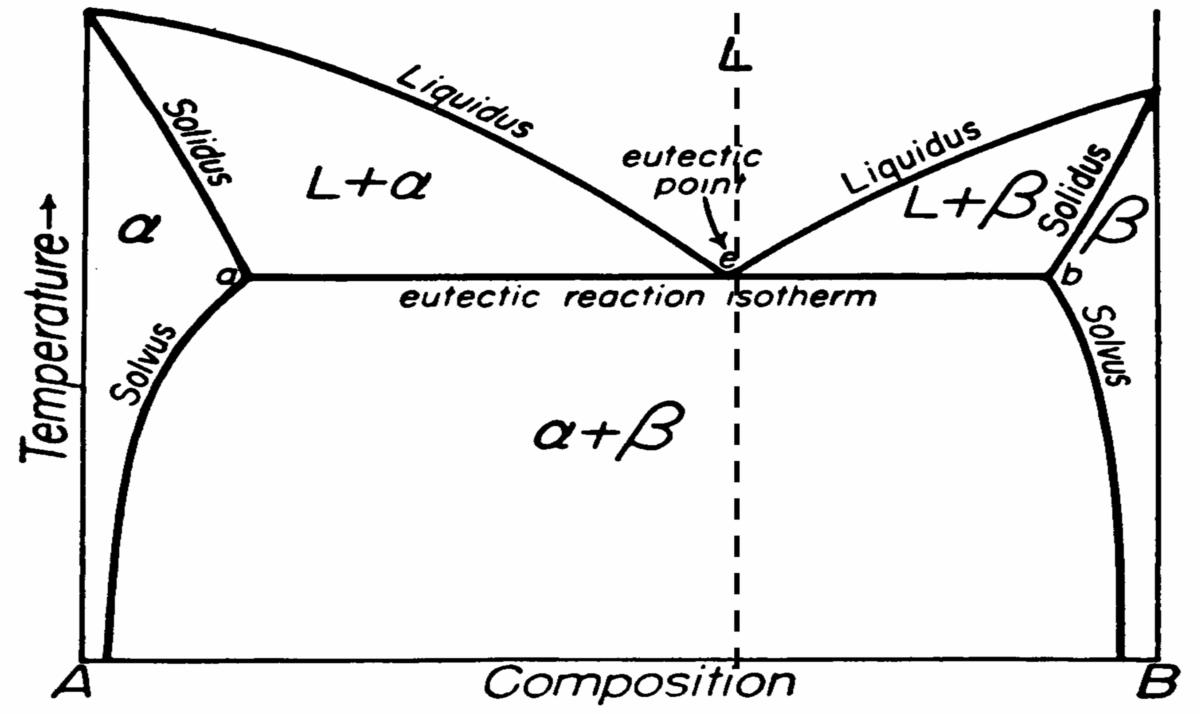


Fig. 4–1

No resfriamento de uma liga de composição eutética através da temperatura eutética ocorre a decomposição do líquido **L** em duas fases sólidas α e β. No aquecimento, as fases α e β reagem para formar o líquido de composição dada pelo ponto eutético. Estas transformações são expressas por

$$\boxed{L \underset{\text{aquecimento}}{\overset{\text{resfriamento}}{\rightleftarrows}} \alpha + \beta}$$

As quantidades relativas das fases α e β, a um infinitésimo de temperatura abaixo da temperatura eutética são dadas por

$$\boxed{\%\alpha = \frac{eb}{ab} \times 100} \qquad \boxed{\%\beta = \frac{ae}{ab} \times 100}$$

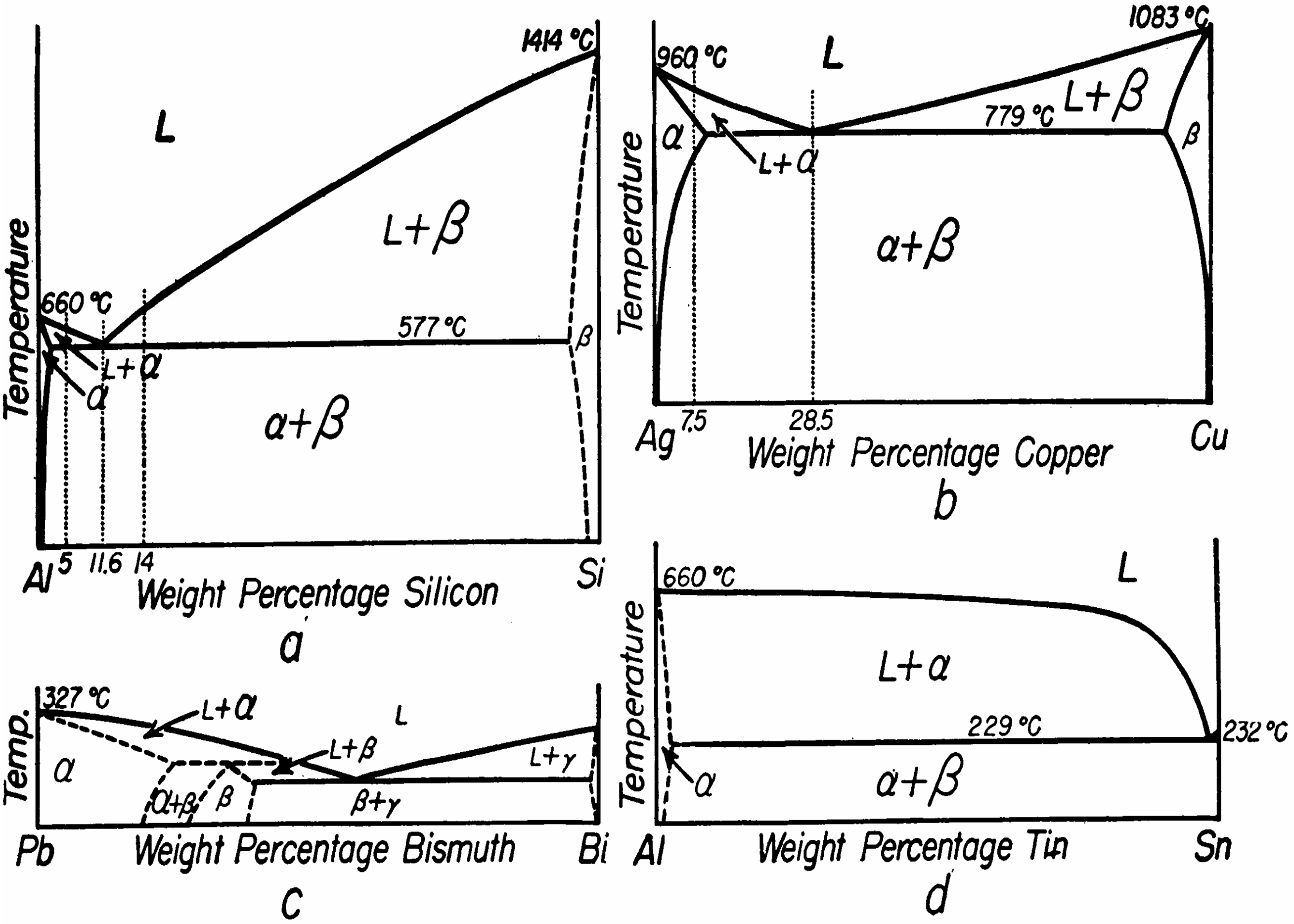


FIG. 4-5. Phase diagrams of some typical eutectic-type systems.

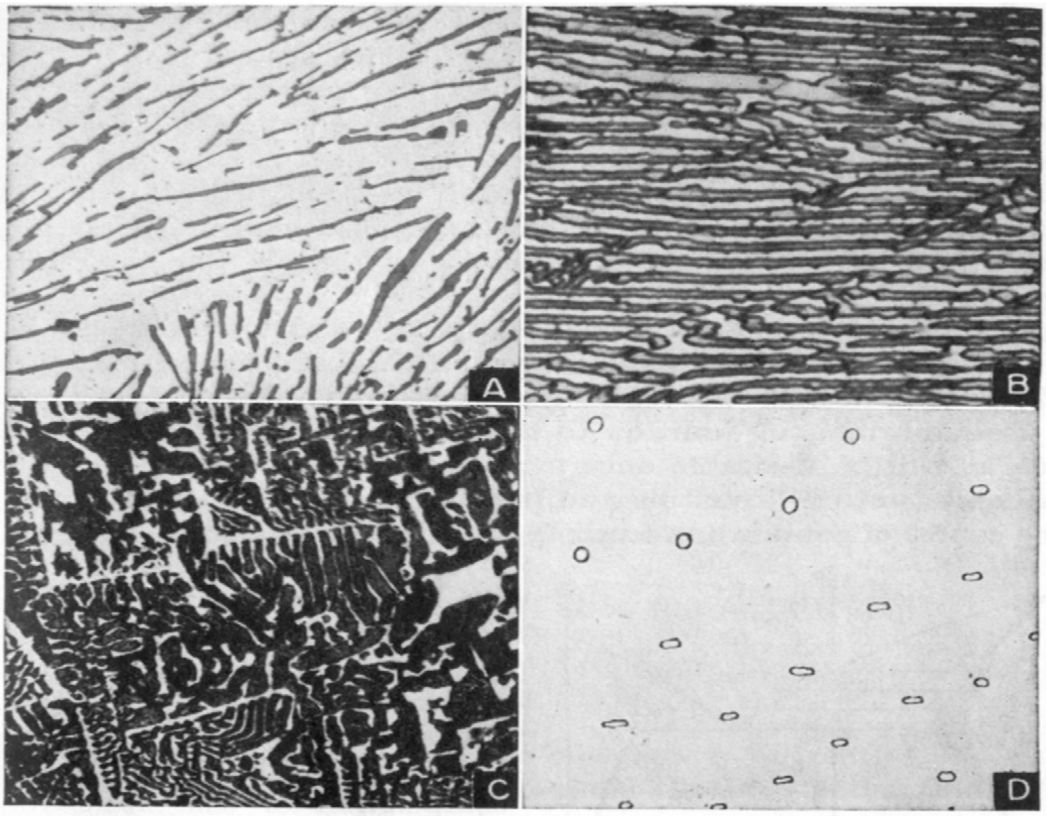
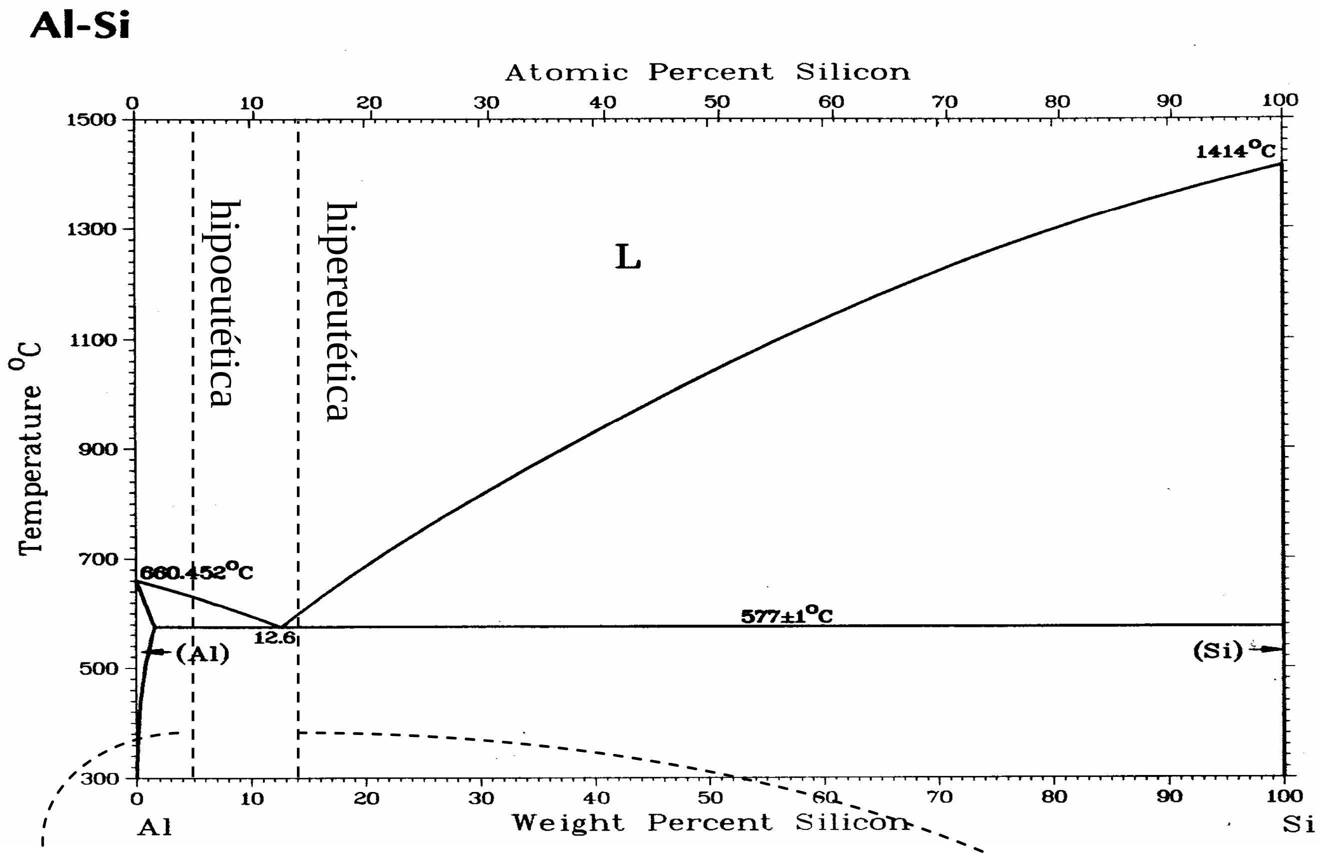


FIG. 4-6. Typical microstructures of some cast eutectic alloys: (*A*) Al-Si 11.6%, magnification 500; (*B*) Ag-Cu 28.5%, magnification 2,000; (*C*) Pb-Bi 56.5%, magnification 100; and (*D*) Al-Sn 99.5%, magnification 650. See also Fig. 4-5.

4.4 - Ligas hipoeutéticas e hipereutética



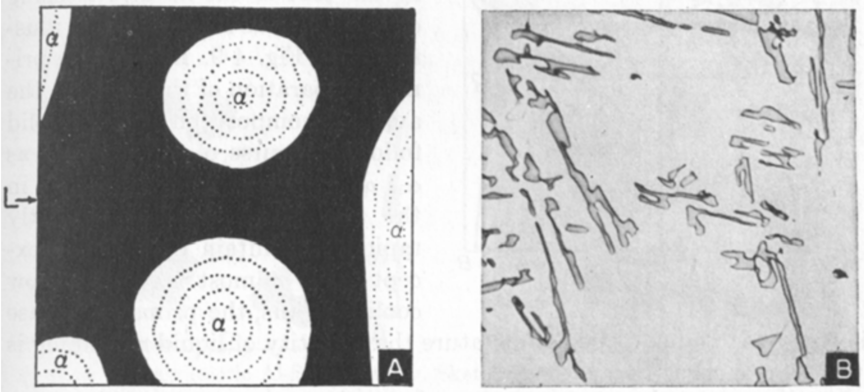


Fig. 4-8. Hypoeutectic Al-Si 5% alloy. Sketch *a* indicates the location of the primary α and the eutectic liquid; the final microstructure at the end of freezing is shown in *b*. Magnification 500.

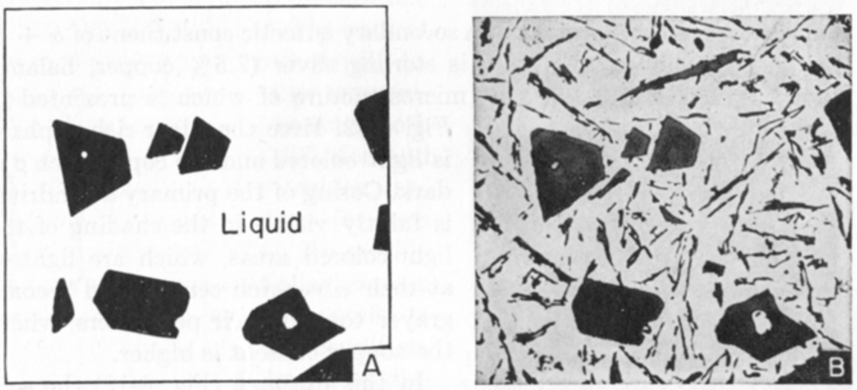
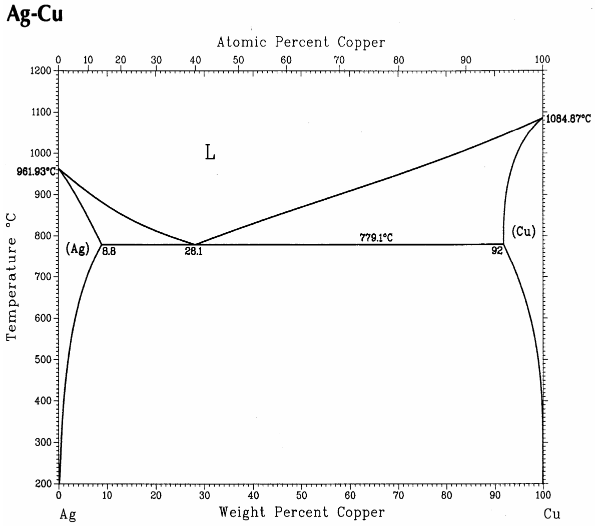


Fig. 4-10. Hypereutectic Al-Si 14% alloy. Sketch *A* shows the location of primary β and the eutectic liquid; photograph *B* shows the final cast microstructure. Magnification 100.

4.5 - Soluções sólidas terminais



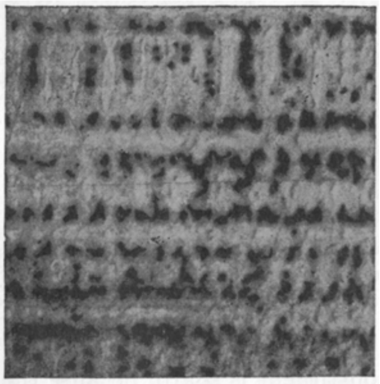


Fig. 4-12. Sterling silver (7.5% Cu) as cast. Light areas, shading from white to light gray, are cored dendrite areas, silver-rich at their centers; dark areas are divorced eutectic. Magnification 100.

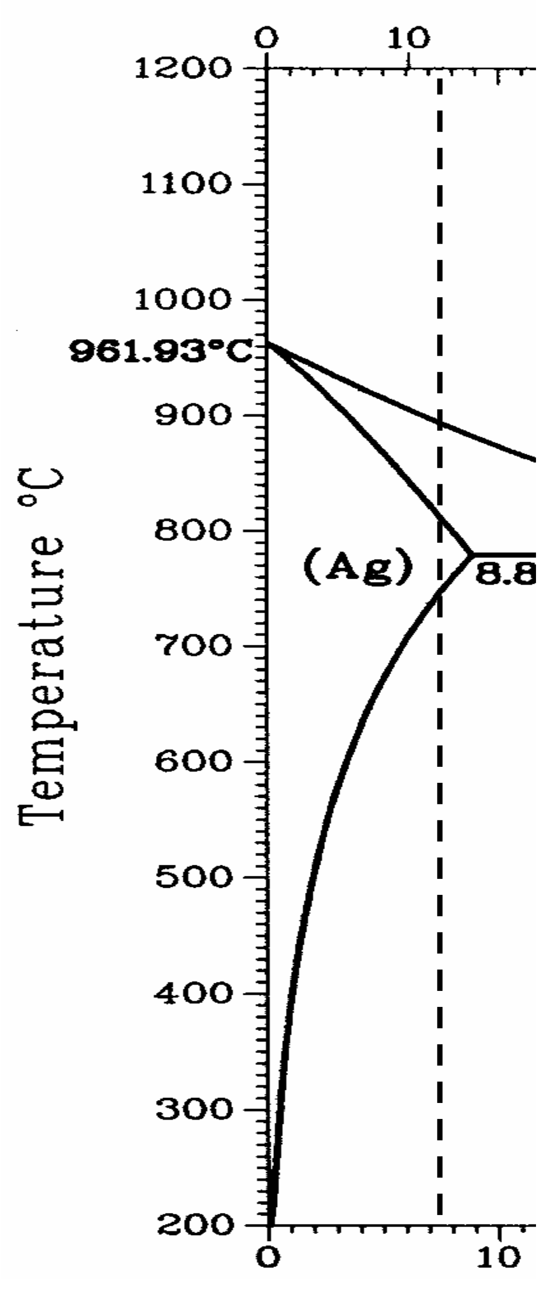
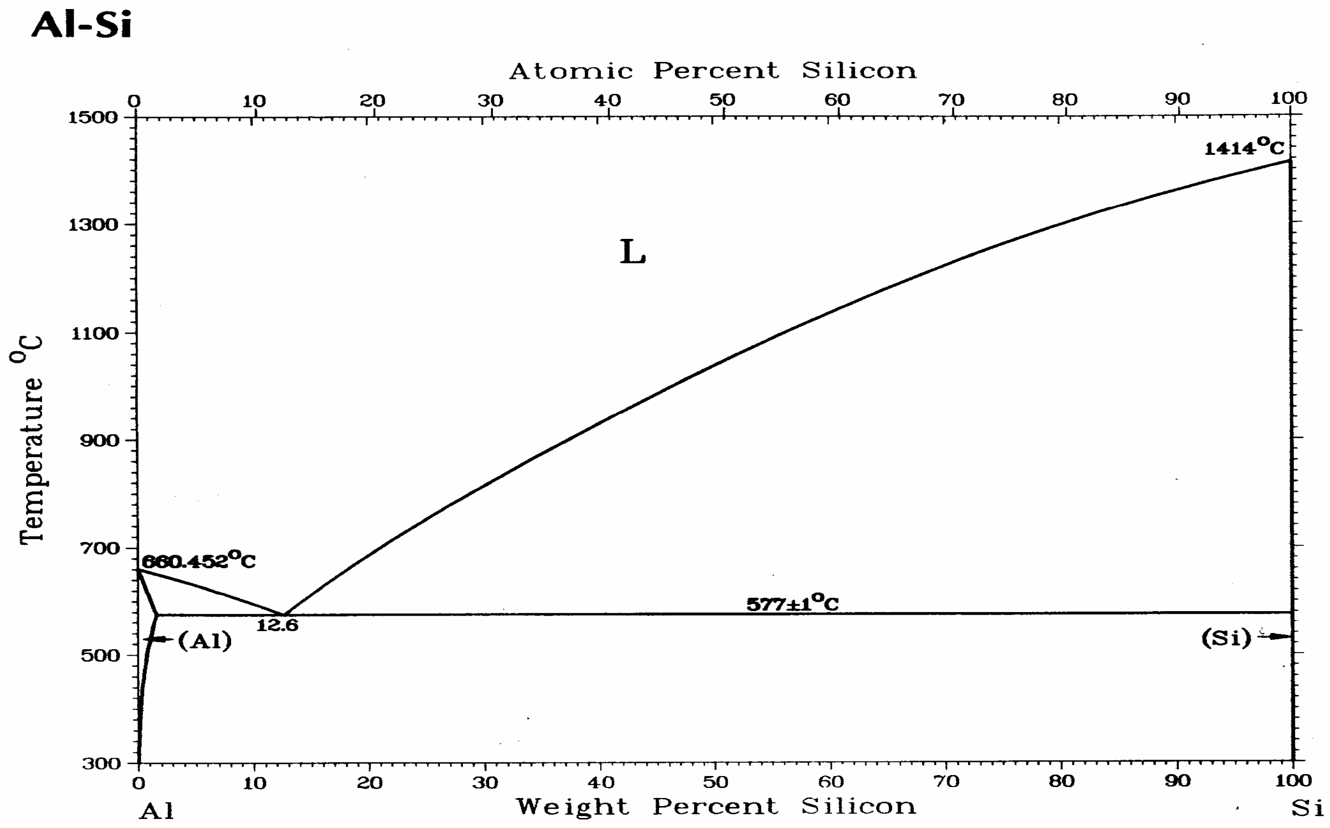
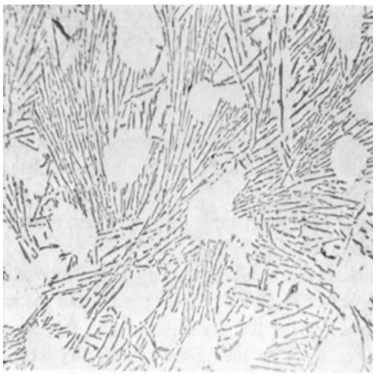


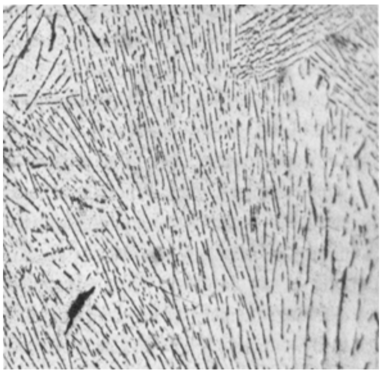
Fig. 4-13. Same as Fig. 4-12, homogenized by heat treatment just below the eutectic temperature and quenched to room temperature; only the silver-rich solid solution is present in this structure. Magnification 100.

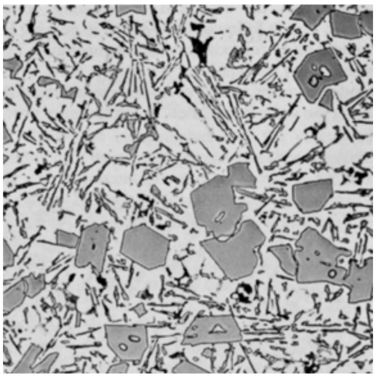
Fig. 4-14. Same as Fig. 4-13, but slowly cooled from the homogenizing temperature. Parallel platelets of copper-rich solid solution have formed upon certain crystallographic planes of the parent silver-rich solid solution, producing a Widmanstätten structure. Magnification 1,000.

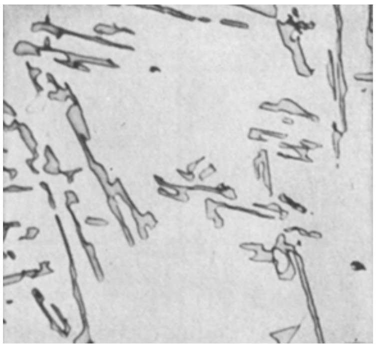
4.6 - Exemplos de microestruturas eutéticas

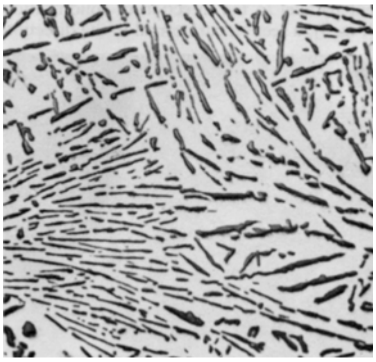


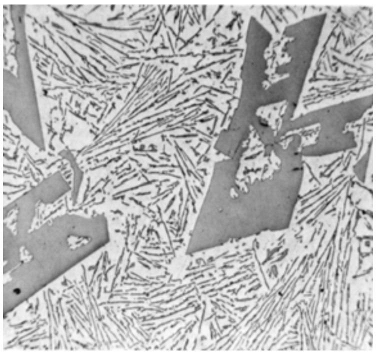




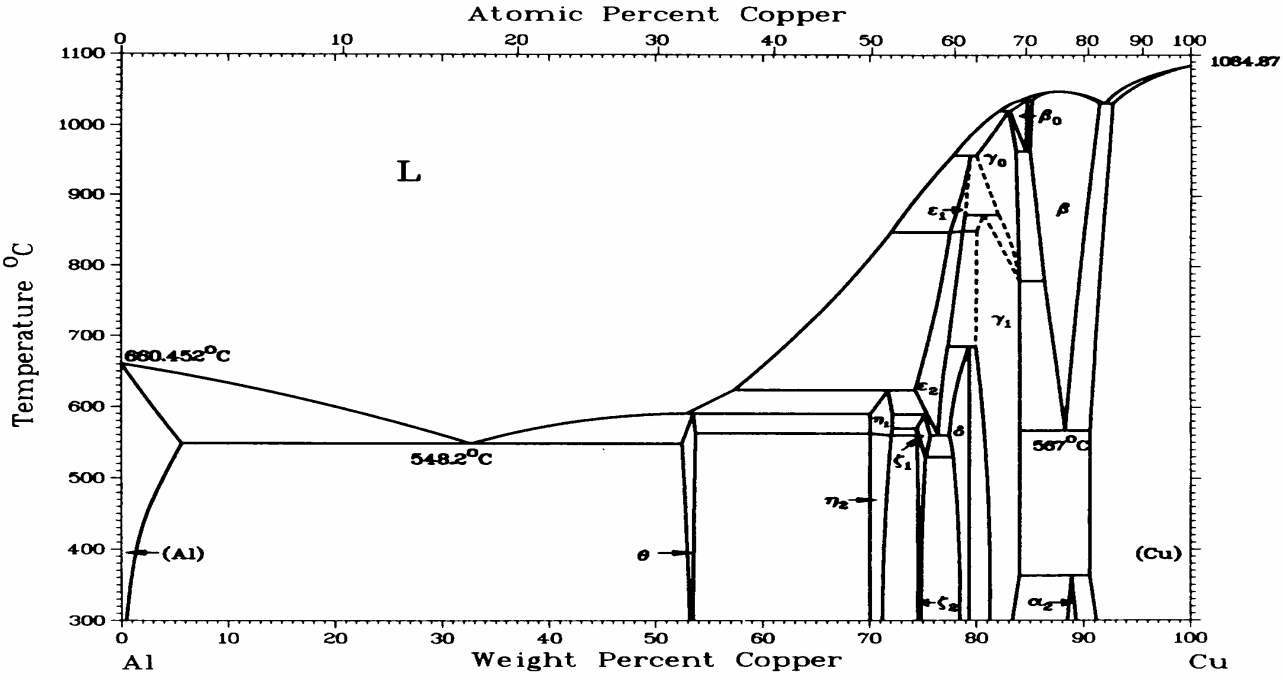


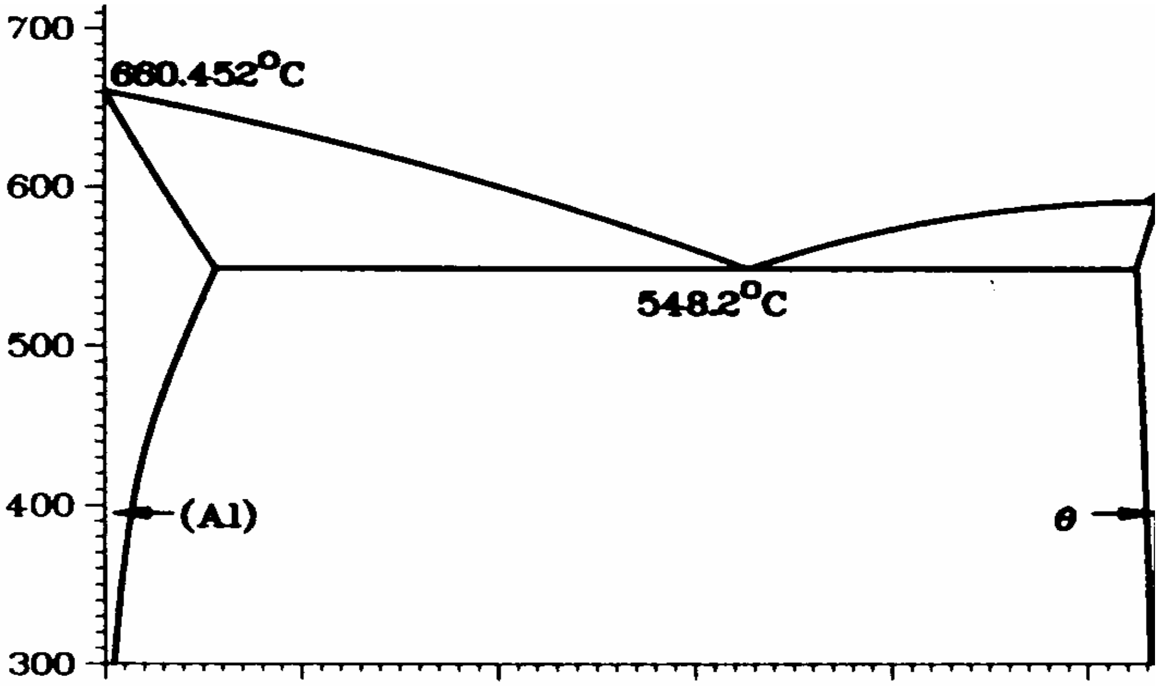






Al-Cu





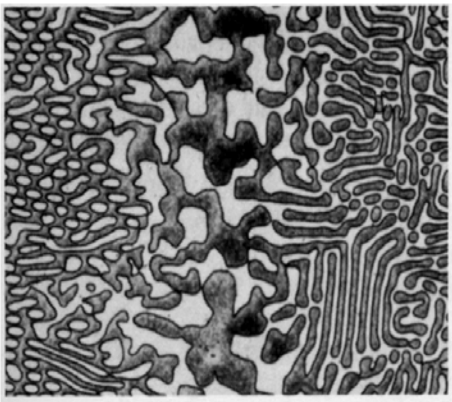


Fig. 17 Interfaces between phases in a reversible-matrix, aluminum-copper eutectic alloy. Etchant and magnification not reported

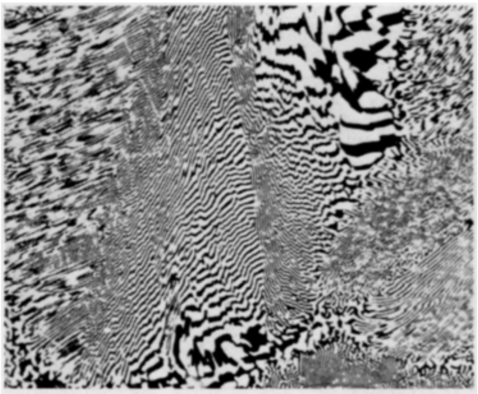


Fig. 10 Colony structure of a $CuAl_2$-Al lamellar eutectic in a casting that was not unidirectionally solidified. Section shows the honeycomb pattern (where section is normal to direction of solidification) and the fanlike arrangement (where section is parallel to direction of solidification). As-polished. 250×

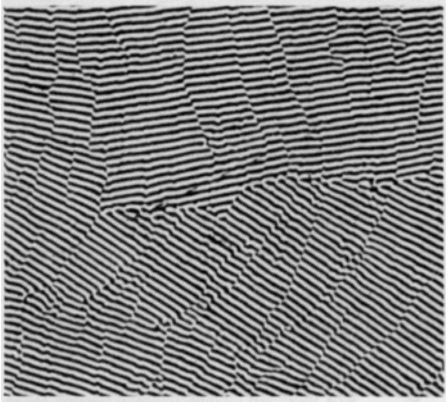
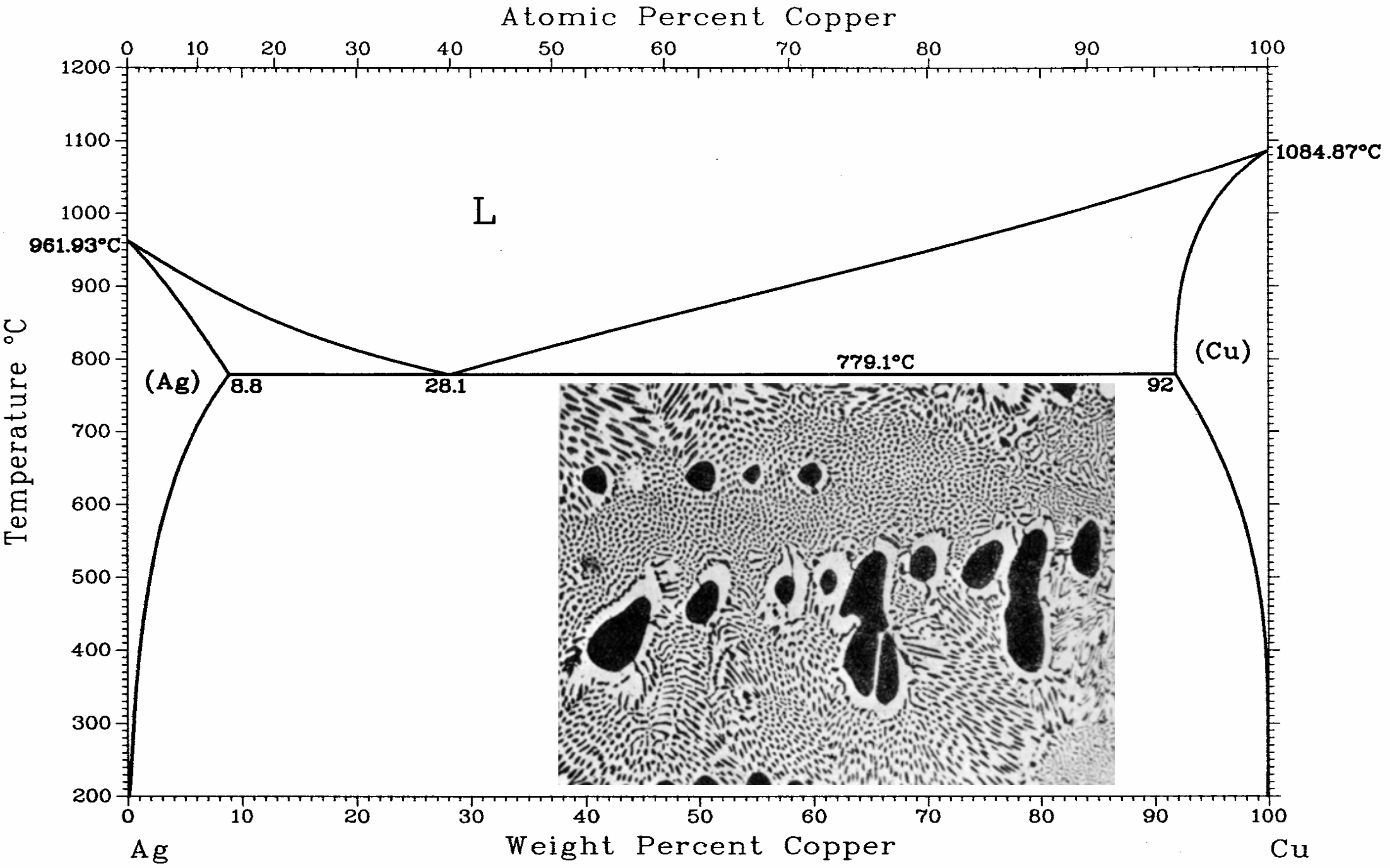


Fig. 11 Lower magnification view of a $CuAl_2$-Al lamellar eutectic in a casting that was solidified unidirectionally showing difficulty of identifying the grain structure of this eutectic. The two "grains" at right (lamellae at about 40° to one another) merge into one "grain" at left. As-polished. 180×

Ag-Cu



Mg-Sn

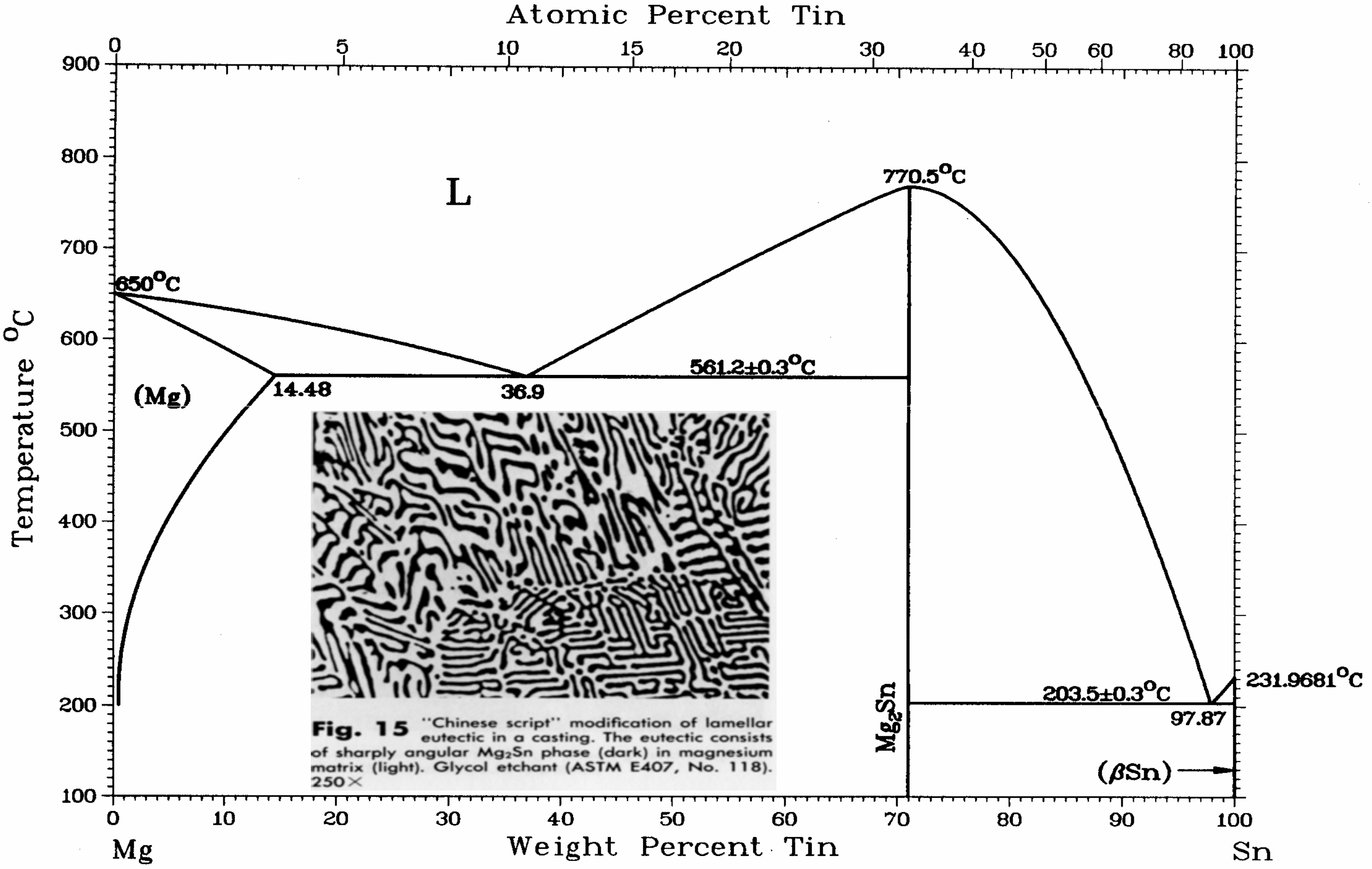


Fig. 15 "Chinese script" modification of lamellar eutectic in a casting. The eutectic consists of sharply angular Mg_2Sn phase (dark) in magnesium matrix (light). Glycol etchant (ASTM E407, No. 118). 250×

4.7 - Solidificação unidirecional com eutéticos

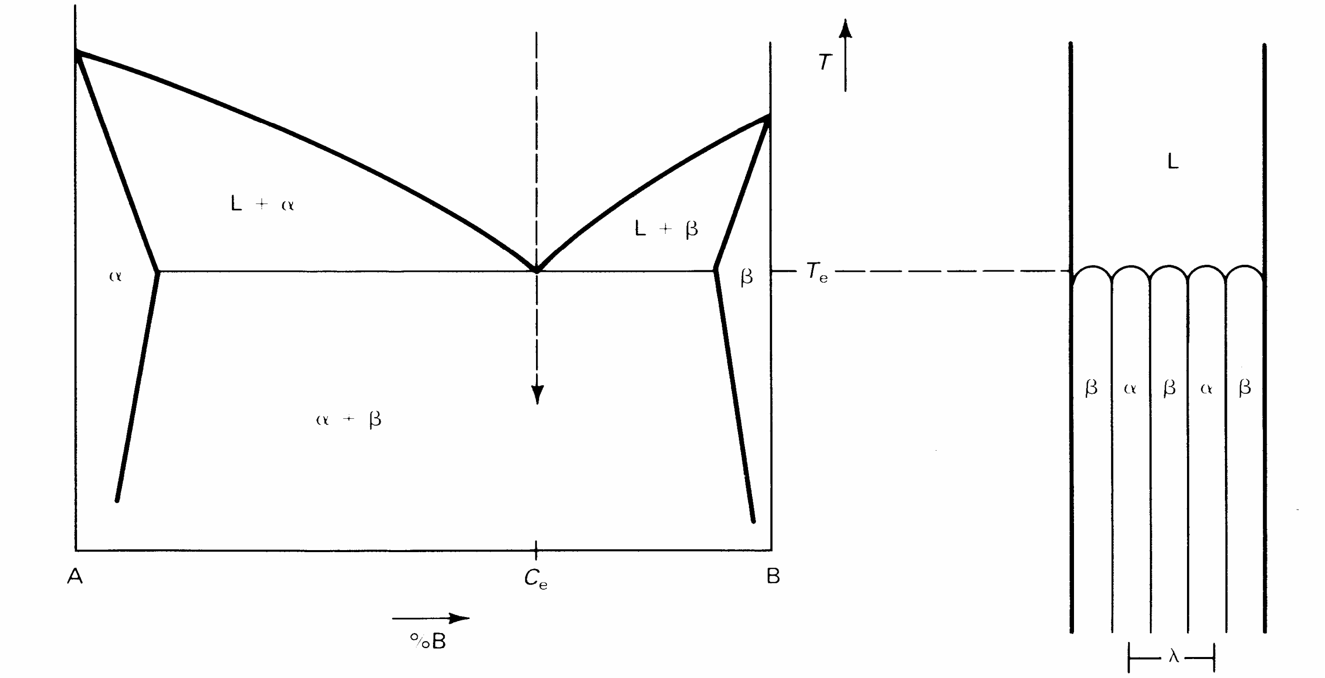


Fig. 1 Phase diagram for a eutectic system showing the eutectic invariant point at temperature (T_e) and composition (C_e)

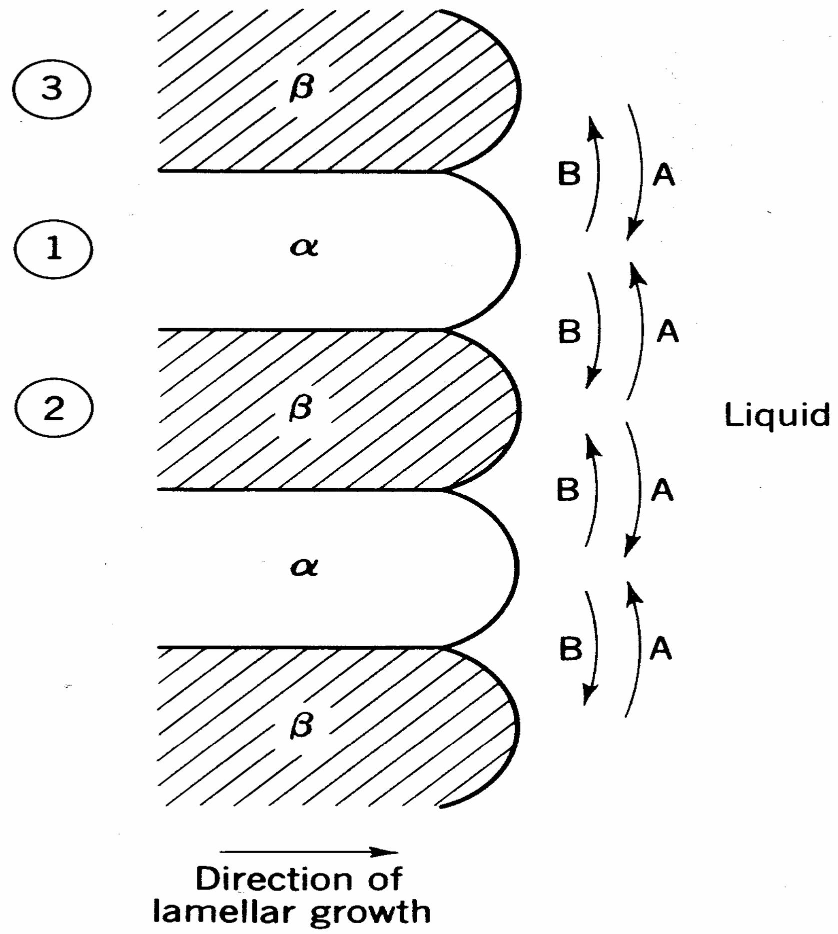


Fig. 6.13 *Lamellar growth in eutectic solidification.*

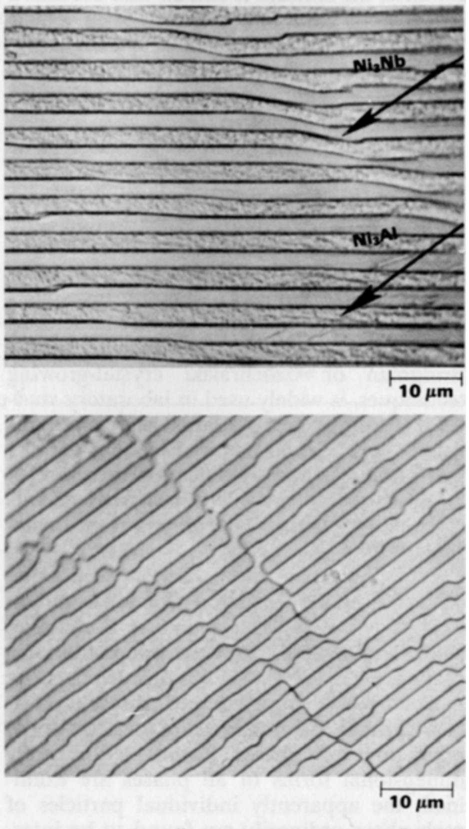


Fig. 4, 5 Lamellar eutectic structures. Fig. 4: Casting of Ni_3Al-Ni_3Nb solidified unidirectionally (left to right). Fig. 5: Same casting as Fig. 4, but a section taken normal to the direction of solidification, showing alternate lamellae of Ni_3Al and Ni_3Nb. Both etched in 5 parts HCl, 1 part HNO_3, 6 parts glycerol. 1000×

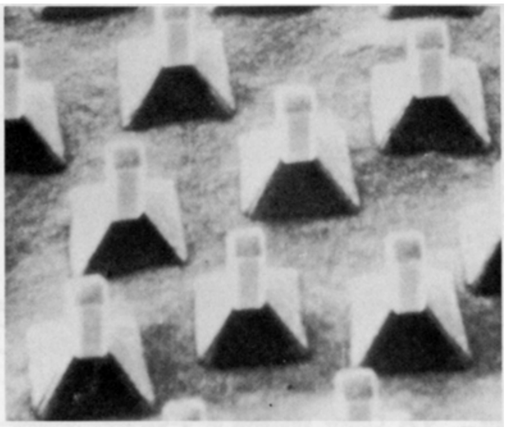


Fig. 7 Scanning electron micrograph of fibrous eutectic unidirectionally solidified vertically. Section shows exposed tantalum carbide particles in a superalloy nickel matrix. Etchant not identified. 40 000×. (M. Henry)

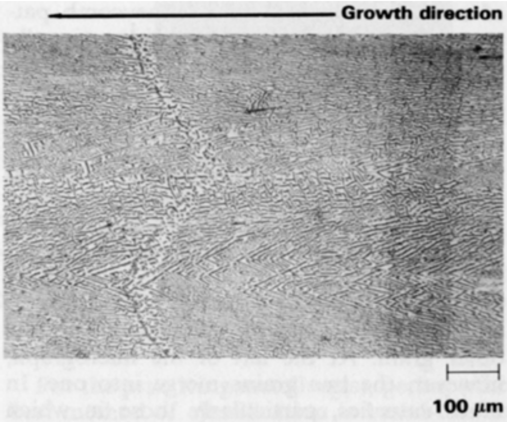


Fig. 8 Colony structure of rod eutectic that was solidified unidirectionally (right to left). Section parallel to direction of growth shows fanlike arrangement of niobium carbide rods (dark) in nickel matrix (light) resulting from curved liquid-solid interface. Murakami's reagent. 30×

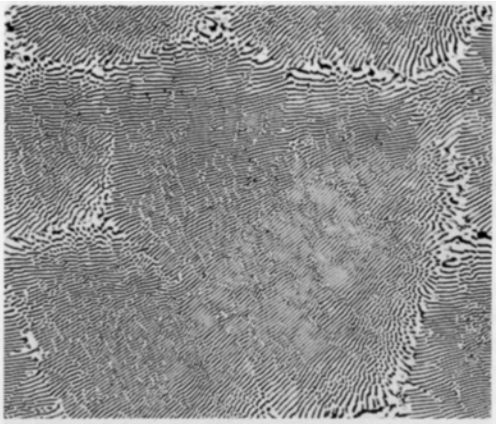


Fig. 9 Colony structure of a lamellar eutectic that was solidified unidirectionally. Section taken normal to the direction of solidification showing the honeycomb pattern of the colonies, which were formed when constitutional undercooling caused the freezing face to be cellular in shape, rather than essentially planar. Dark and light layers in each colony are Mg_2Al_3 phase and aluminum, respectively. Etchant not identified. 200×

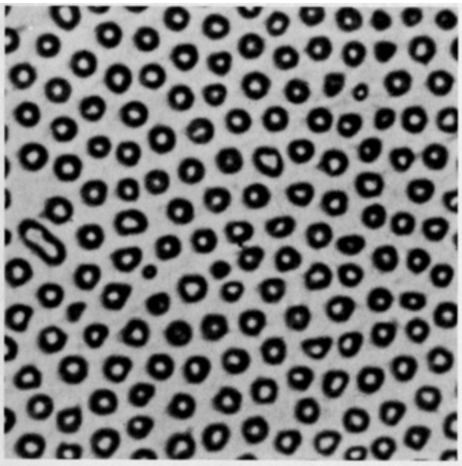


Fig. 26 Transverse section through parallel rods in a unidirectionally solidified Mg-32Al eutectic alloy. Growth rate was 1.5×10^{-2} mm/s (6×10^{-4} in./s). Temperature gradient was 3.7 °C/mm (1.7 °F/10^{-2}in.). Etchant and magnification not reported. (Ref 17)

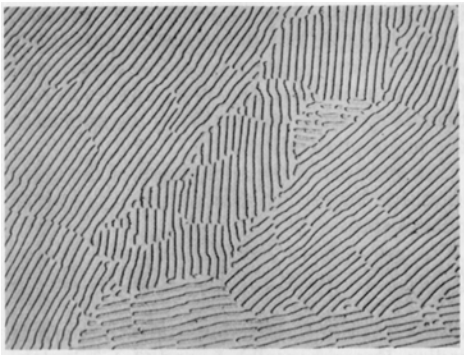


Fig. 31 Lamellae in a unidirectionally solidified aluminum-copper eutectic alloy. Etchant and magnification not reported. (Ref 1)

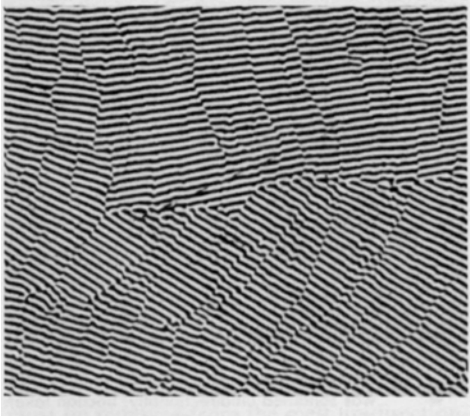
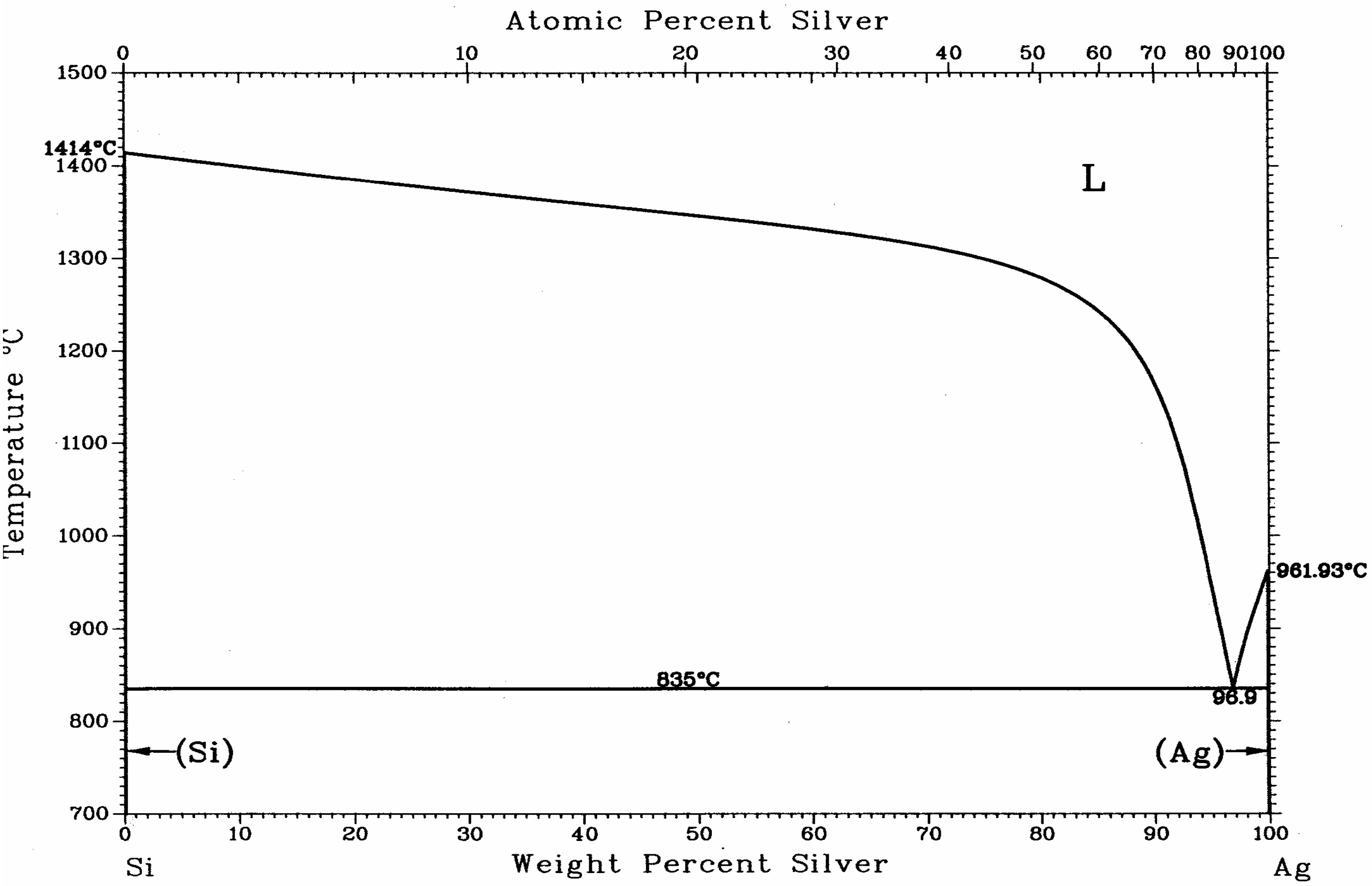


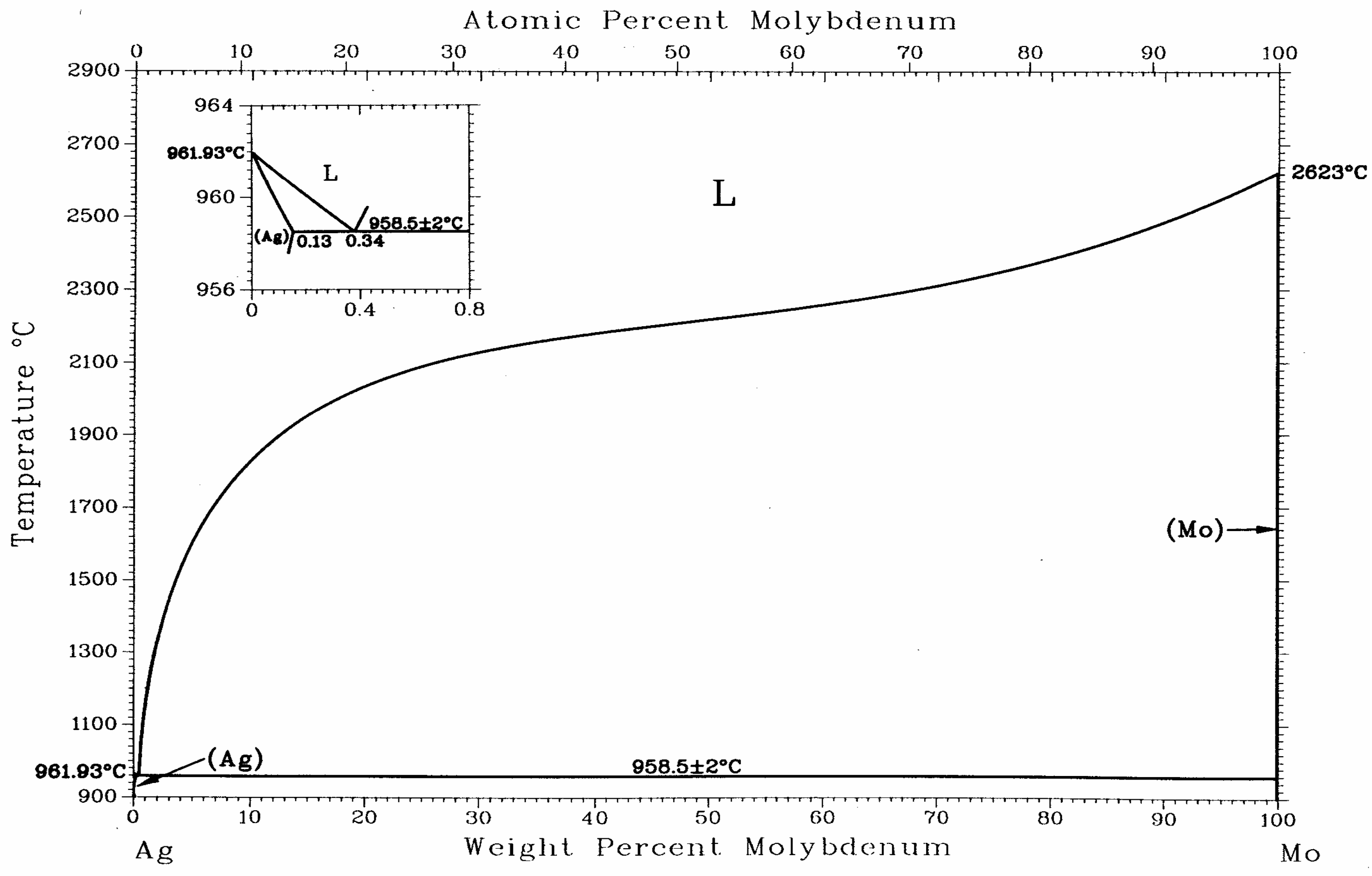
Fig. 11 Lower magnification view of a $CuAl_2$-Al lamellar eutectic in a casting that was solidified unidirectionally showing difficulty of identifying the grain structure of this eutectic. The two "grains" at right (lamellae at about 40° to one another) merge into one "grain" at left. As-polished. 180×

4.8 - Casos limites de eutéticos

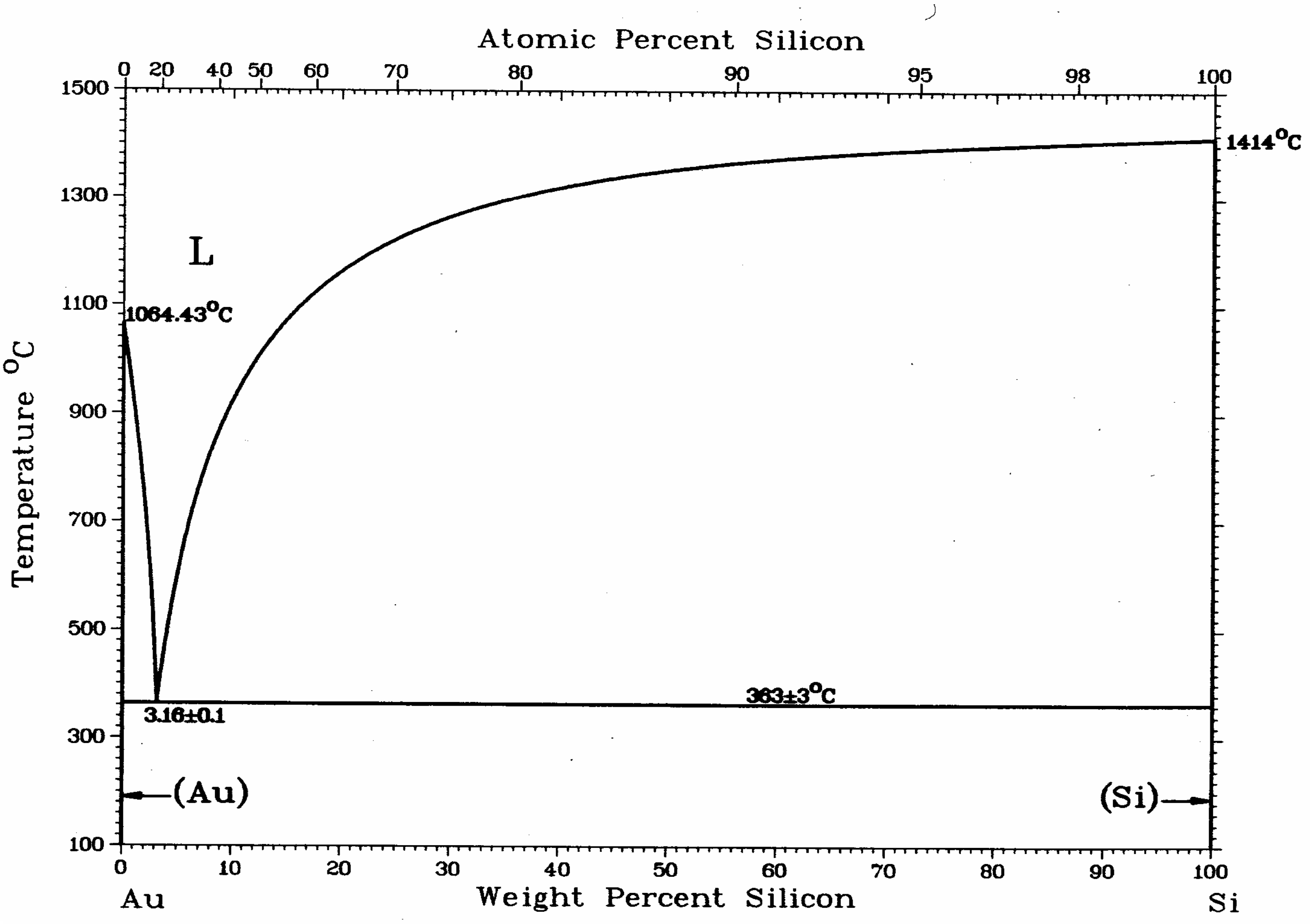
Ag-Si



Ag-Mo

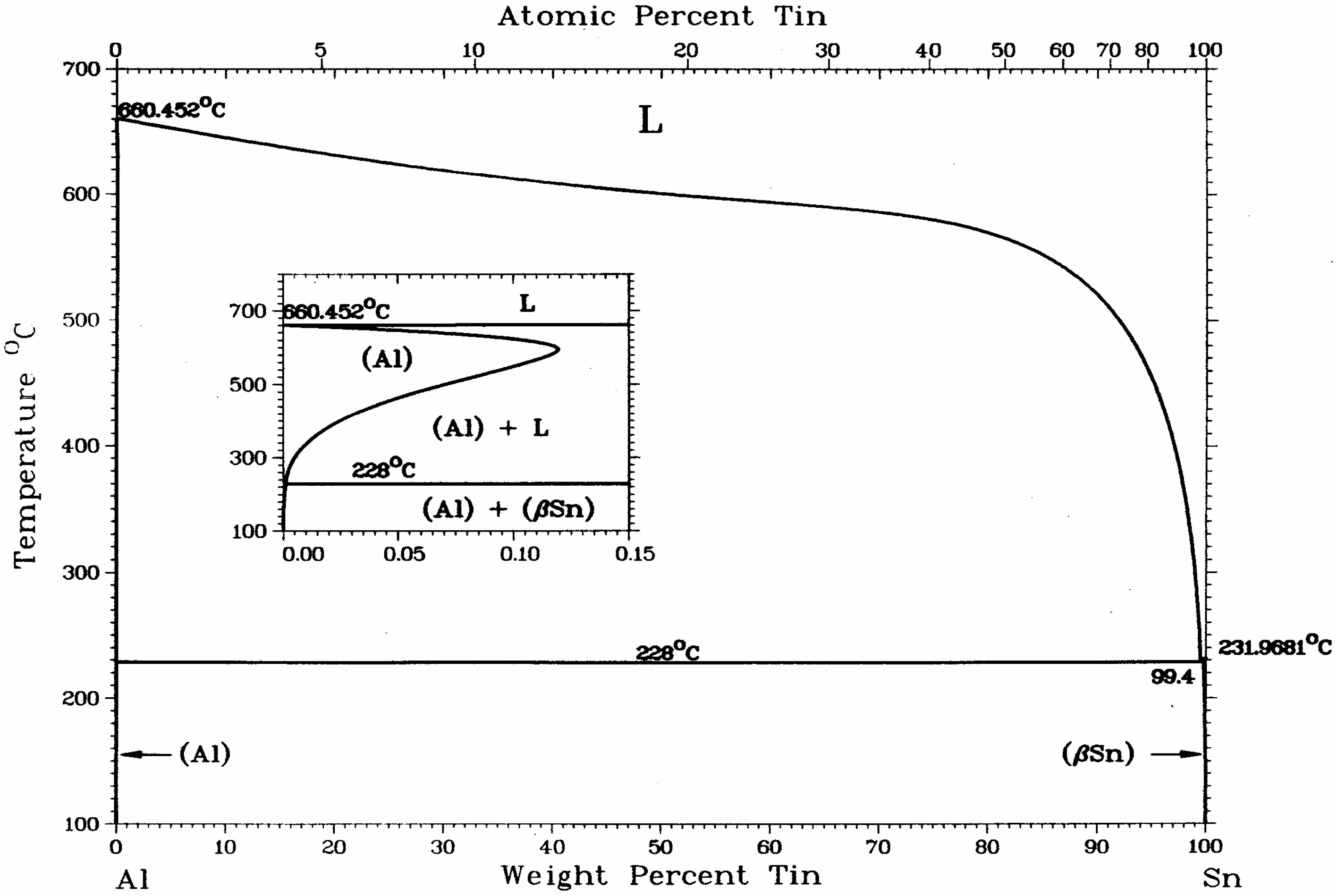


Au-Si



Atomic Percent Silicon
0
20
40
50
60
70
80
90
95
98
100
1500
1300
1100
900
700
500
300
100
Temperature °C
L
1064.43°C
1414°C
363±3°C
3.16±0.1
(Au)
(Si)
0
10
20
30
40
50
60
70
80
90
100
Au
Weight Percent Silicon
Si

Al-Sn



Atomic Percent Tin
0
5
10
20
30
40
50
60
70
80
100
700
600
500
400
300
200
100
Temperature °C
660.452°C
L
228°C
231.9681°C
99.4
(Al)
(βSn)
700
660.452°C
L
(Al)
500
(Al) + L
300
228°C
(Al) + (βSn)
100
0.00
0.05
0.10
0.15
0
10
20
30
40
50
60
70
80
90
100
Al
Weight Percent Tin
Sn

4.9 - Exercícios

1 - Em um sistema A-B as composições das três fases em equilíbrio na temperatura de transformação eutética são:
α = 15%B; L = 75%B e β = 95%B.
Assumindo a solidificação em equilíbrio de uma liga composta de iguais partes de A e B a uma temperatura infinitesimalmente abaixo daquela do eutético, calcule:
a) as percentagens de α primário e de eutético $\alpha + \beta$,
b) as percentagens de α total e β total.

2 - Desenhe um diagrama eutético para o seguinte caso:
- A funde a 1000^{o}C, B funde a 700^{o}C;
- uma liga de composição 25%B solidifica completamente imediatamente abaixo de 500^{o}C e em equilíbrio é composta de 73,33% de α primária e 26,67% de eutético $\alpha + \beta$;
- uma liga contendo 50%B à mesma temperatura é composta de 40% de α primária e 60% de eutético $\alpha + \beta$, o total de α nesta última liga sendo 50%.

5 - SISTEMAS EUTETÓIDES BINÁRIOS

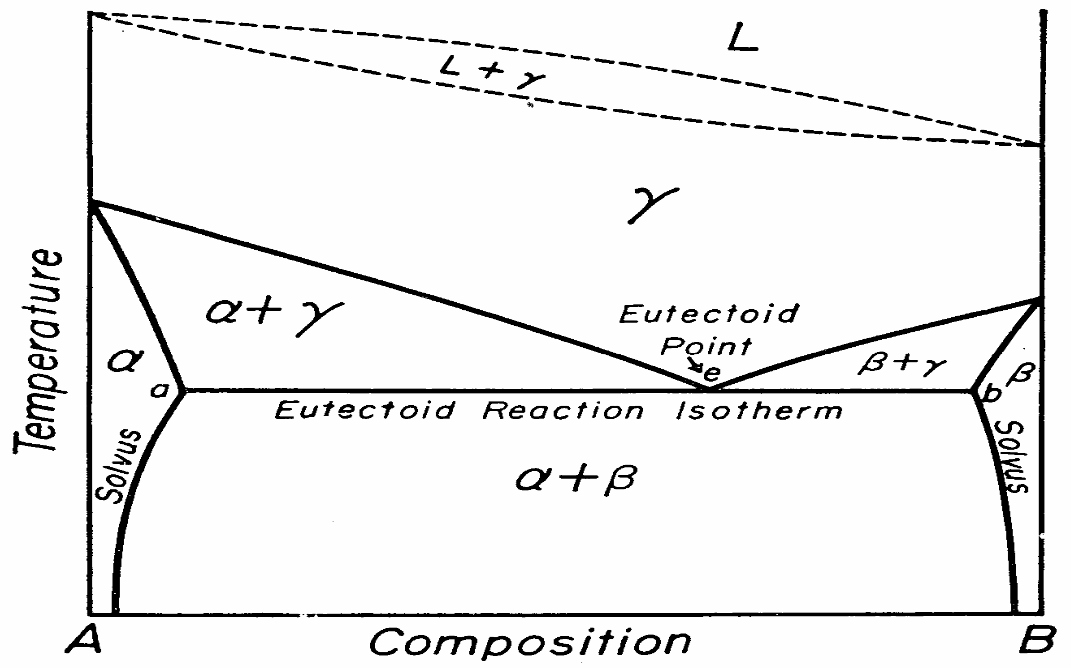


FIG. 5-1

$$\boxed{\gamma \underset{\text{aquecimento}}{\overset{\text{resfriamento}}{\rightleftarrows}} \alpha + \beta}$$

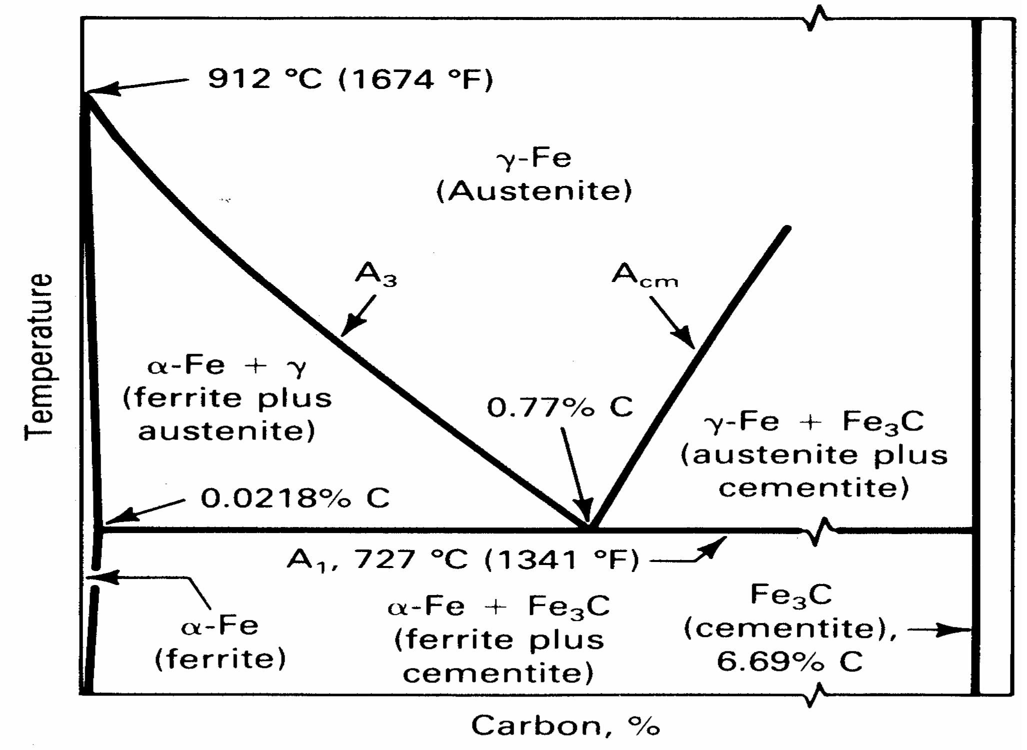


Fig. 2 Eutectoid region of the Fe-Fe_3C phase diagram

5.1 - Aplicação da regra das fases

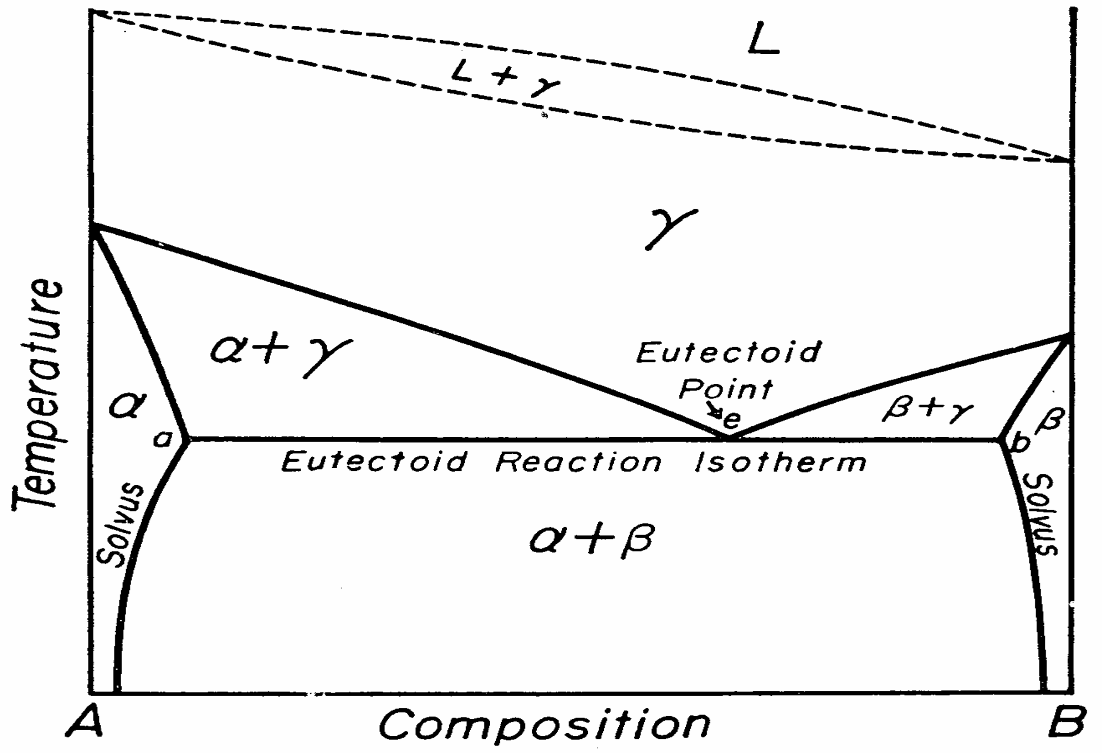


FIG. 5-1

$P + F = C + \mathbf{1}$
(*pressão constante*)

- <u>equilíbrio invariante</u>:
  $F = 0$; $C = 2$; $\boldsymbol{P = 3}$
  (dado pela linha eutetóide "**a-e-b**")

- <u>equilíbrio univariante</u>:
  $F = 1$; $C = 2$; $\boldsymbol{P = 2}$
  (regiões γ+α, γ+β e α+β)

- <u>equilíbrio bivariante</u>:
  $F = 2$; $C = 2$; $\boldsymbol{P = 1}$
  (regiões marcadas como α, β e γ)

5.2 - Liga de composição eutetóide

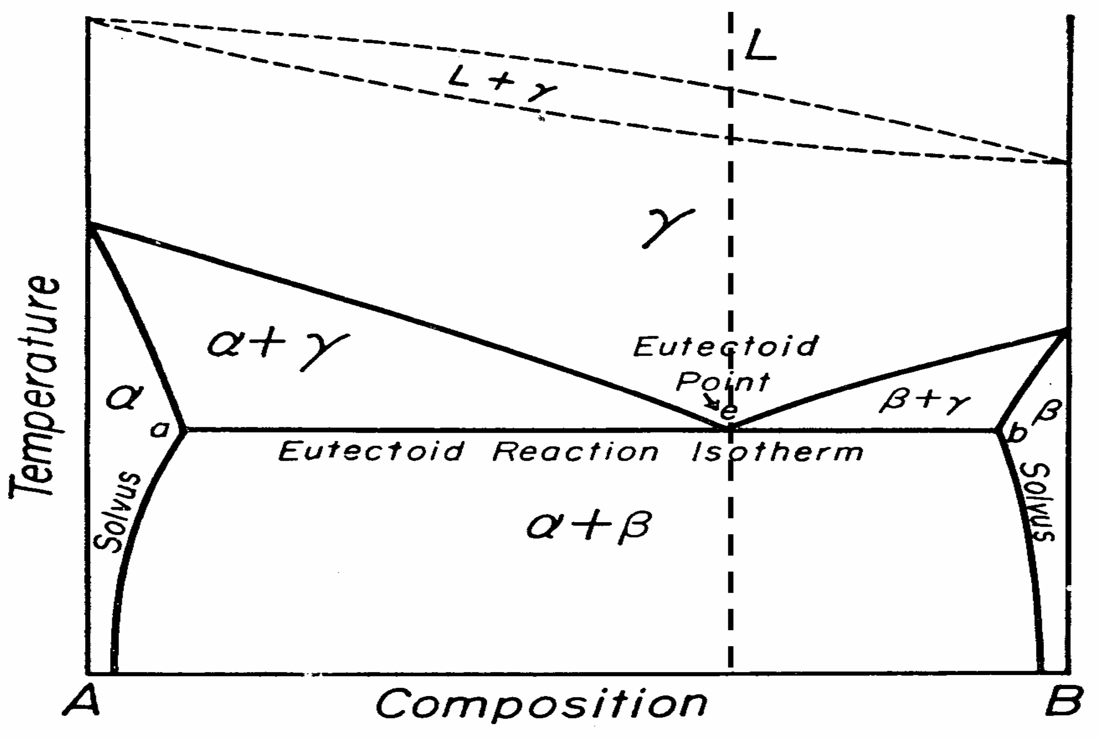


FIG. 5-1

No resfriamento de uma liga de composição eutetóide através da temperatura eutetóide ocorre a decomposição da fase sólida γ em duas outras fases sólidas α e β. No aquecimento, as fases α e β reagem para formar a fase γ de composição dada pelo ponto eutetóide. Estas transformações são expressas por

$$\boxed{\gamma \underset{\text{aquecimento}}{\overset{\text{resfriamento}}{\rightleftarrows}} \alpha + \beta}$$

As quantidades relativas das fases α e β, a um infinitésimo de temperatura abaixo da temperatura eutetóide são dadas por

$$\boxed{\%\alpha = \frac{eb}{ab} \times 100} \qquad \boxed{\%\beta = \frac{ae}{ab} \times 100}$$

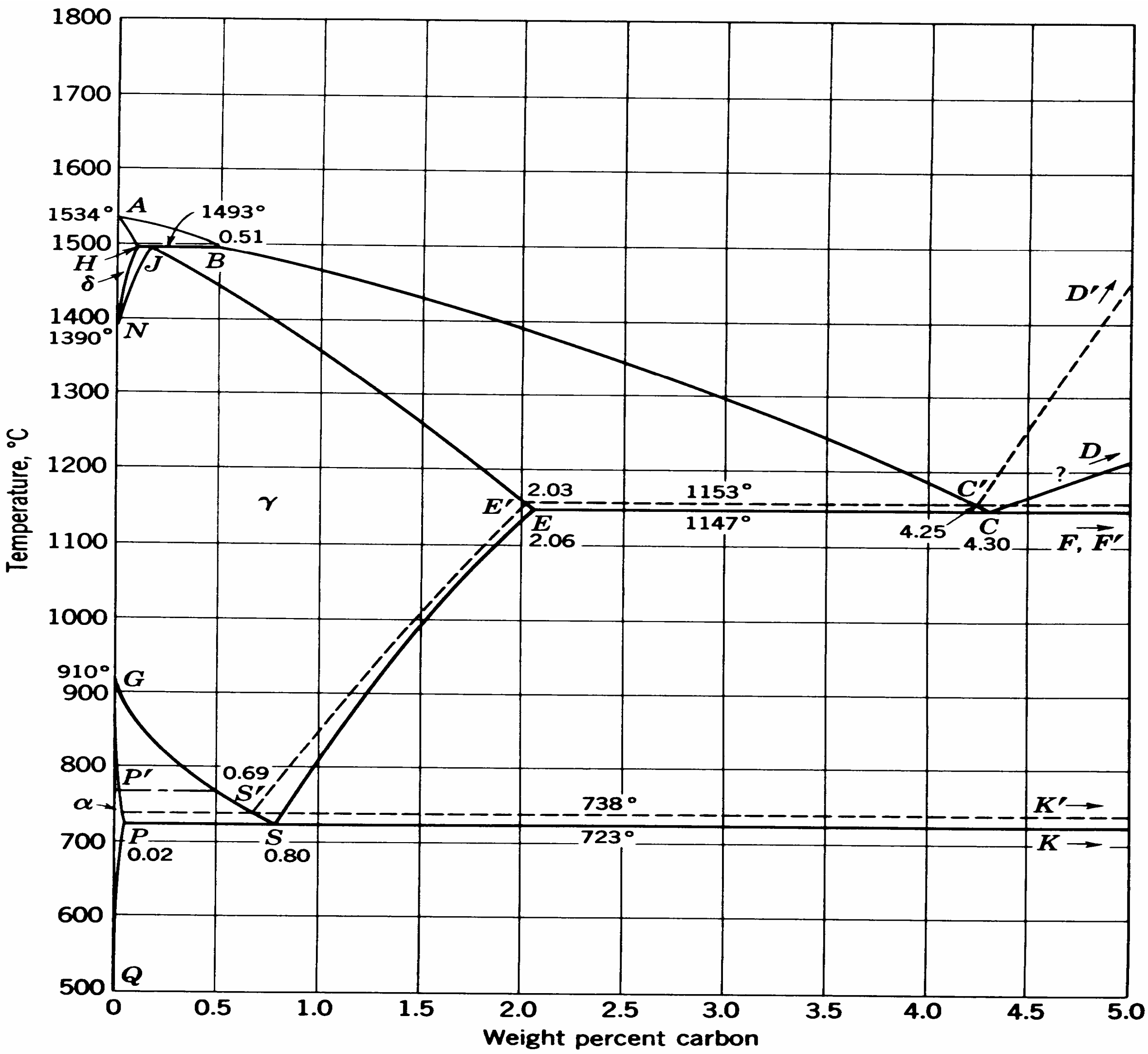
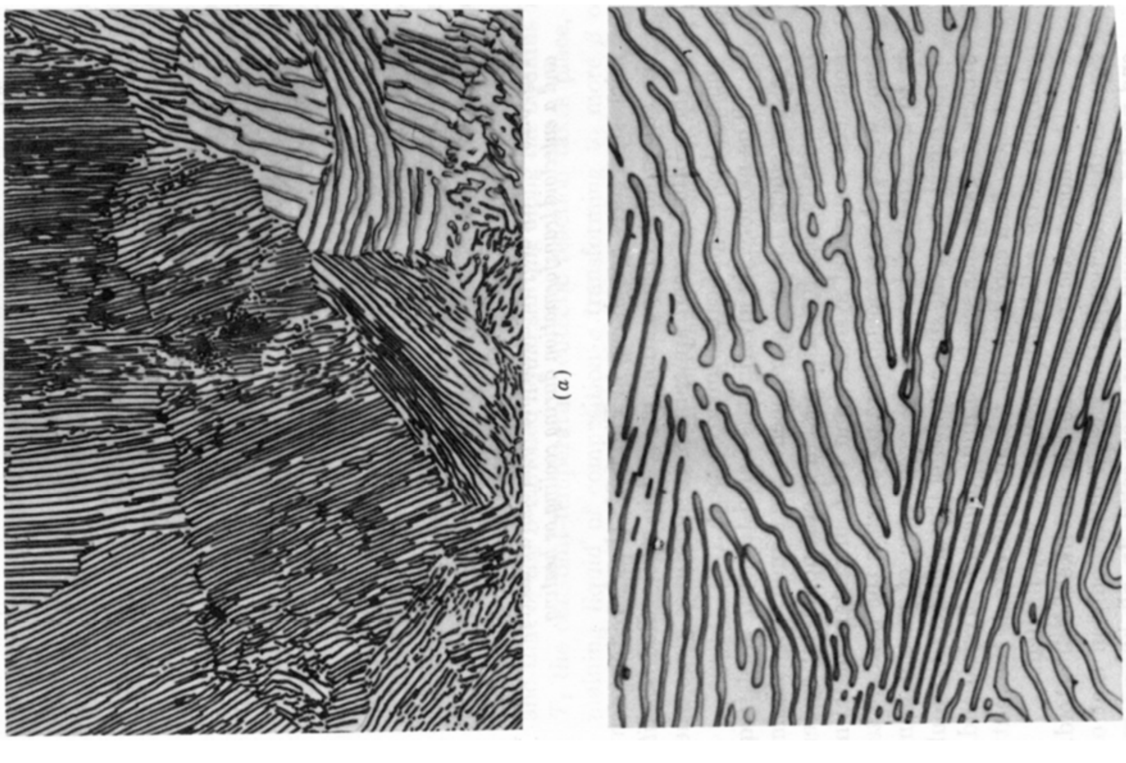


Fig. 6.25 *The iron-carbon phase diagram. (From Hansen.*[4.17]*)*


(*a*)

(*b*)

Fig. 6.22 *The microstructure of pearlite,* (*a*) *1000×;* (*b*) *2500×. (From Bain and Paxton, "Alloying Elements in Steel," ASM. Courtesy J. R. Villela and H. C. Knechtel, Edgar C. Bain Laboratory for Fundamental Research, United States Steel Corp., Monroeville, Pa.)*

5.3 - Ligas hipoeutetóides e hipereutetóides

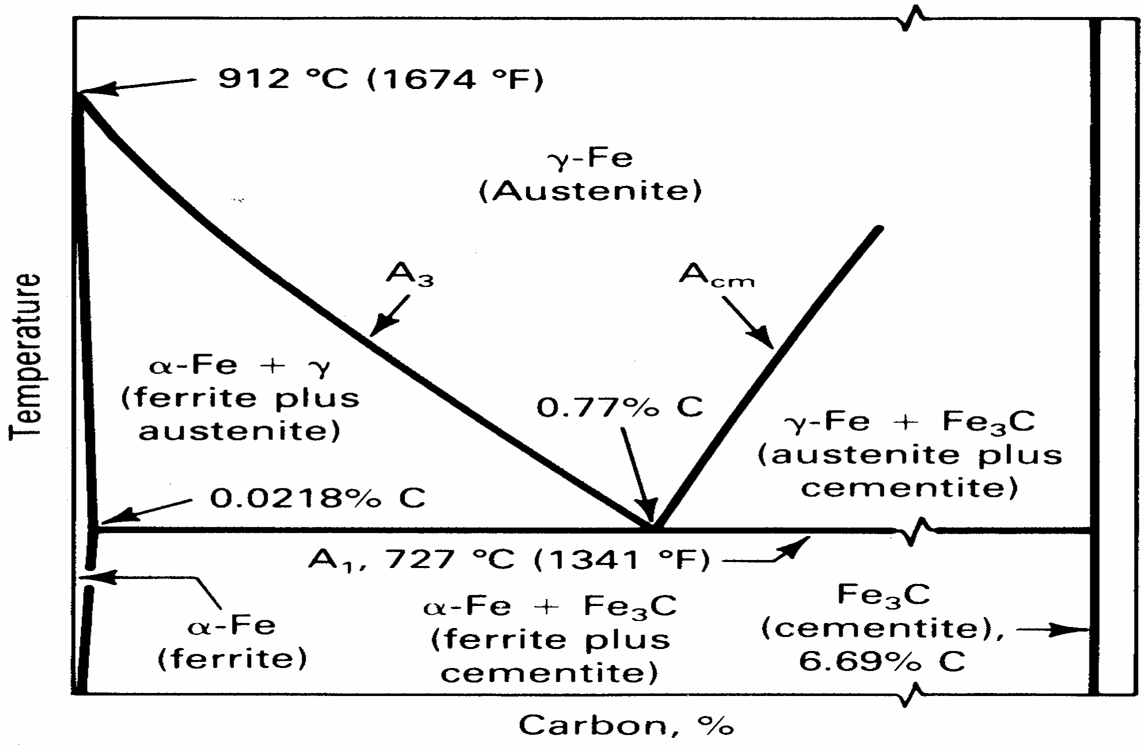


Fig. 2 Eutectoid region of the Fe-Fe_3C phase diagram

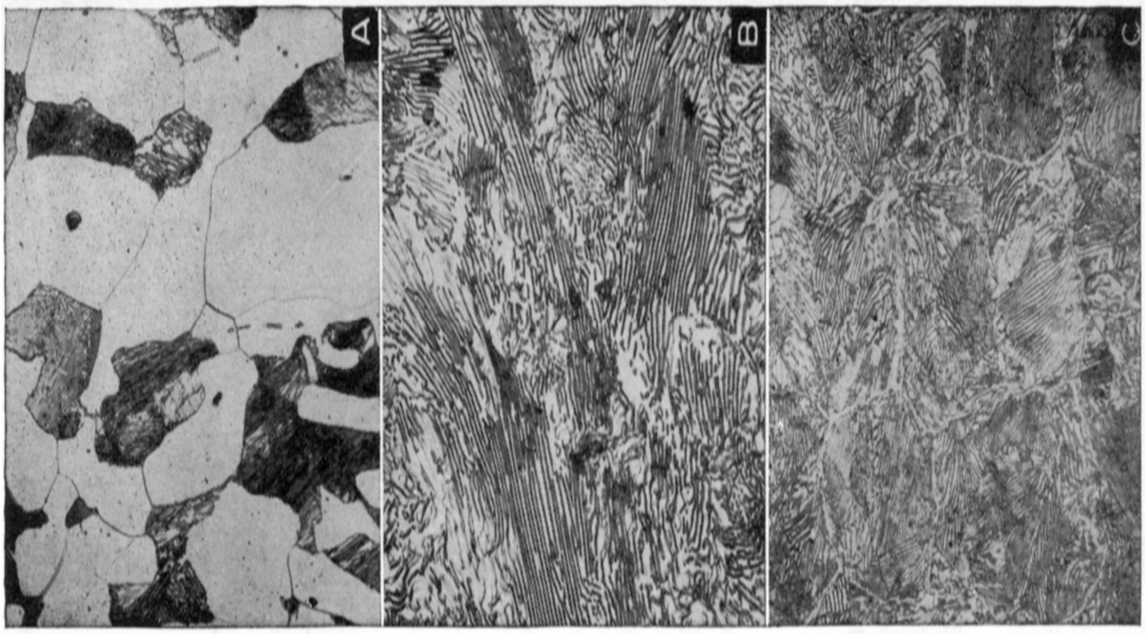
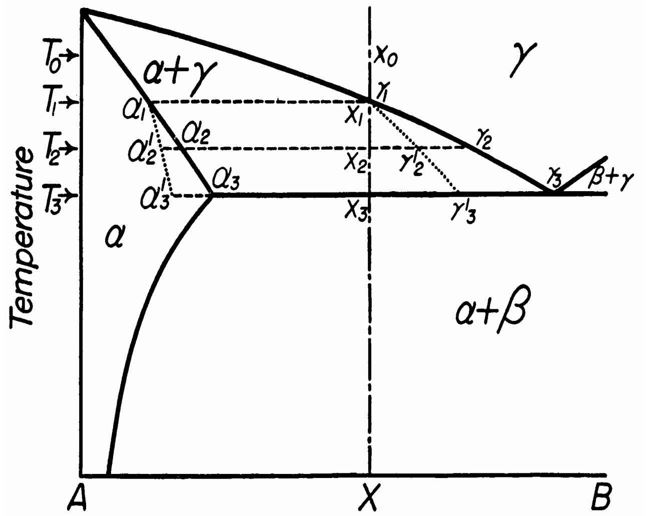


FIG. 5-3. (*A*) Hypoeutectoid steel, 0.3% C. Light areas are proeutectoid ferrite (α); dark areas are the pearlitic eutectoid constituent ($\alpha + Fe_3C$). Magnification 500. (*B*) Eutectoid steel, 0.8% carbon, typical pearlite ($\alpha + Fe_3C$). Magnification 500. (*C*) Hypereutectoid steel, 1.2% C. Thin bands of proeutectoid cementite (Fe_3C), light gray, outline the grains of pearlitic eutectoid constituent ($\alpha + Fe_3C$). Magnification 500.

5.4 - Transformação fora do equilíbrio



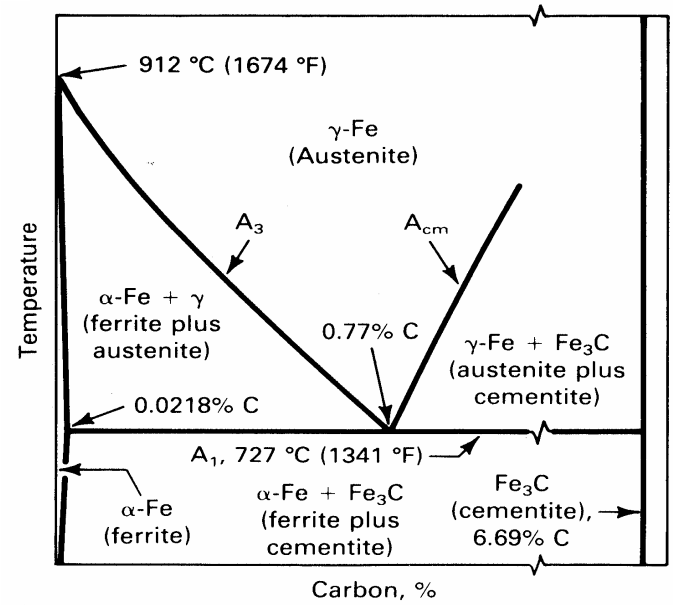


Fig. 2 Eutectoid region of the Fe-Fe_3C phase diagram

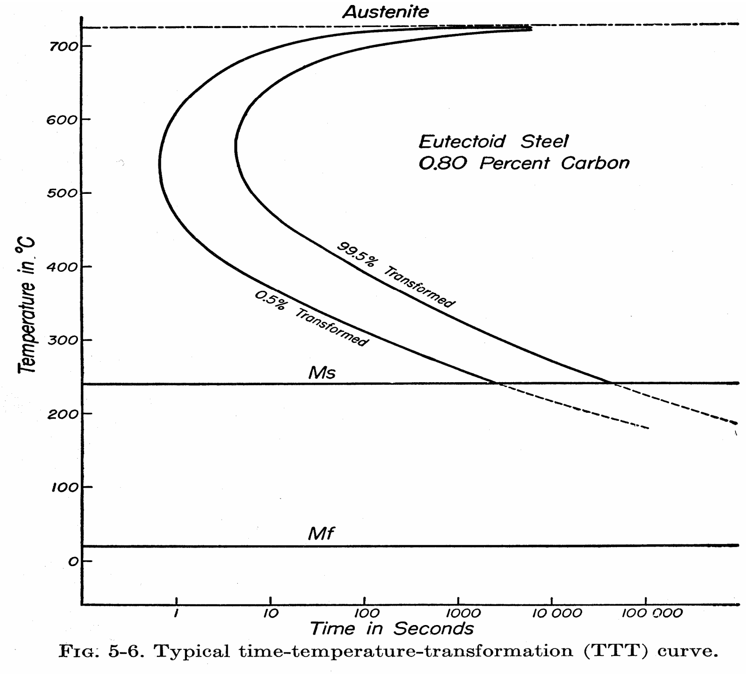


FIG. 5-6. Typical time-temperature-transformation (TTT) curve.

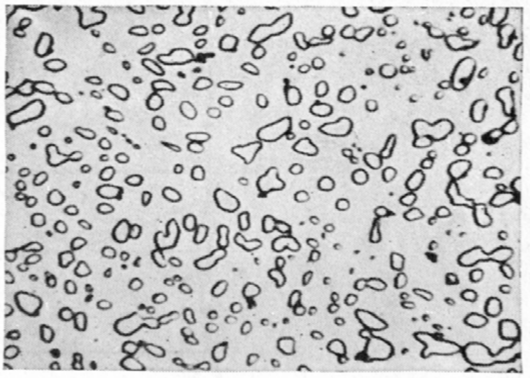


FIG. 5-13. Eutectoid steel in which the Fe_3C has been spheroidized by long heating at a temperature slightly below that of the eutectoid equilibrium; compare with Fig. 5-5A. Magnification 1,500.

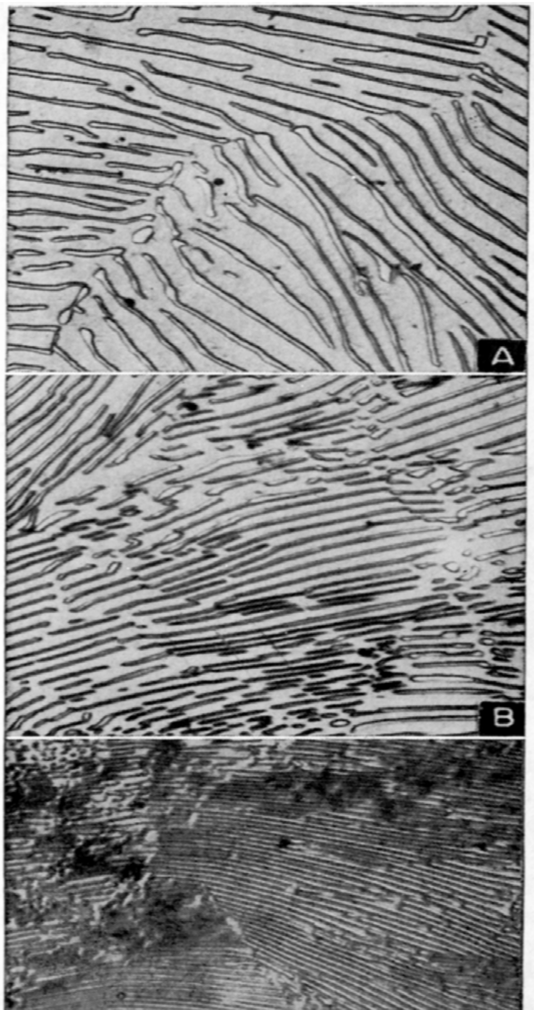
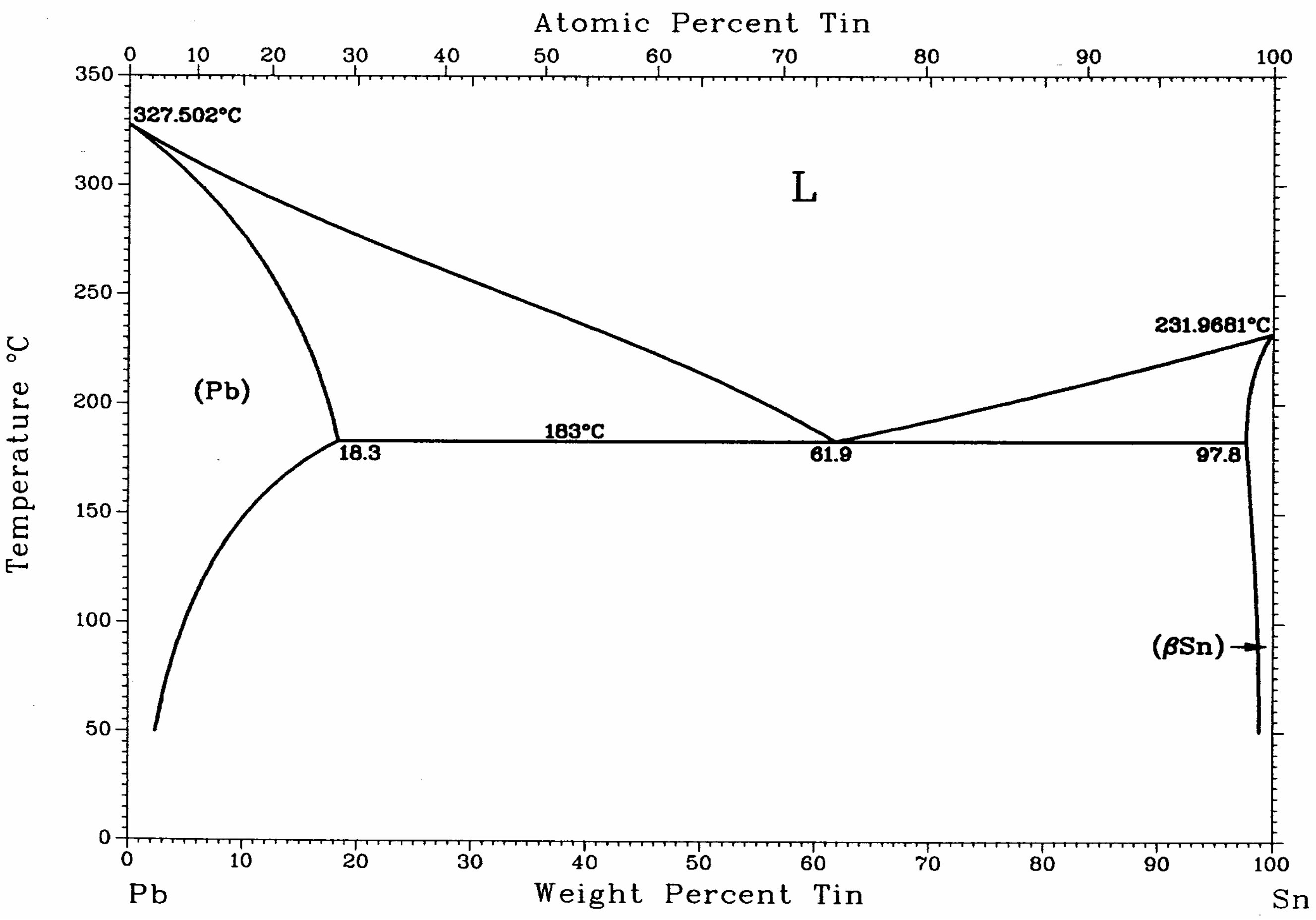


FIG. 5-5. Illustrates the variation in pearlite lamella spacing with temperature of formation: (A) formed at the highest temperature, (B) formed at an intermediate temperature, and (C) formed at the lowest temperature Magnification 1,500.

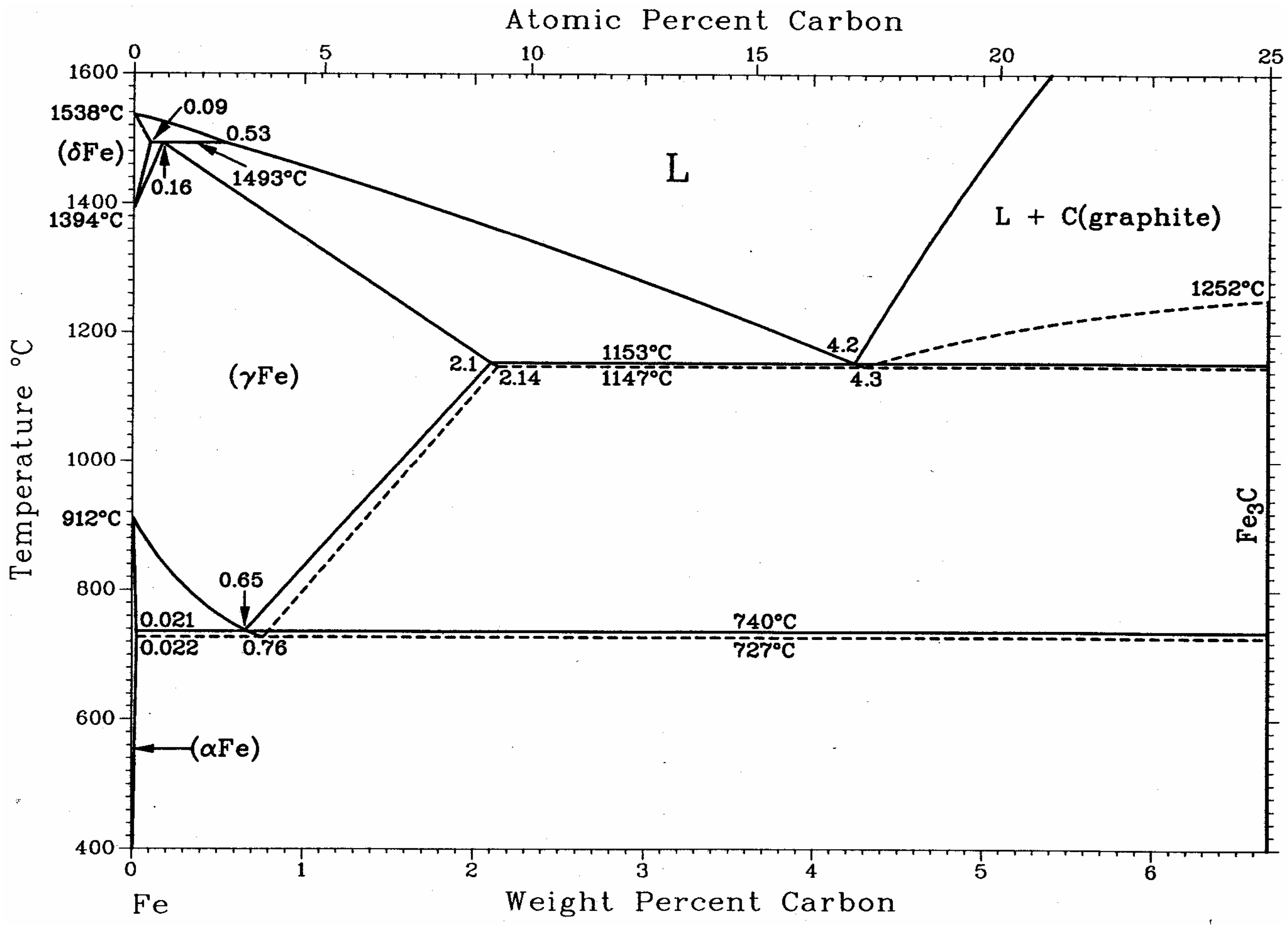
EXERCÍCIOS

Pb-Sn



* Para uma liga com 40%Sn-60%Pb a 150^{o}C,
  a) Qual(quais) fase(s) está(ão) presente(s) neste equilíbrio e qual o grau de liberdade do sistema nestas condições?
  b) Quais as quantidades relativas de α e β em peso e volume, considerando as densidades de α=11,2g/cm^3 e β=7,3g/cm^3?
  c) Com o aquecimento em equilíbrio desta liga, em qual temperatura aparecem os primeiros sinais da fase líquida? Qual a composição deste líquido? em qual temperatura ocorre a fusão total da liga? qual a composição do último sólido presente antes da fusão total da liga?

* Uma amostra de 1,5kg de uma liga contendo 90%Pb-10%Sn é aquecida a 250^{o}C, sendo nesta temperatura composta inteiramente de solução sólida α. A liga deve ser levada a um estado tal que seja composta de 50% em peso de fase líquida e o restante de α. Isto pode ser conseguido tanto pelo aquecimento da liga dada quanto pela variação de composição à temperatura constante. Para isso, pergunta-se:
  a) A qual temperatura deve-se aquecer a amostra?
  b) Quanto Sn deve ser adicionado aos 1,5kg da liga a 250^{o}C?



* Calcule as frações mássicas de ferrita e cementita na perlita.

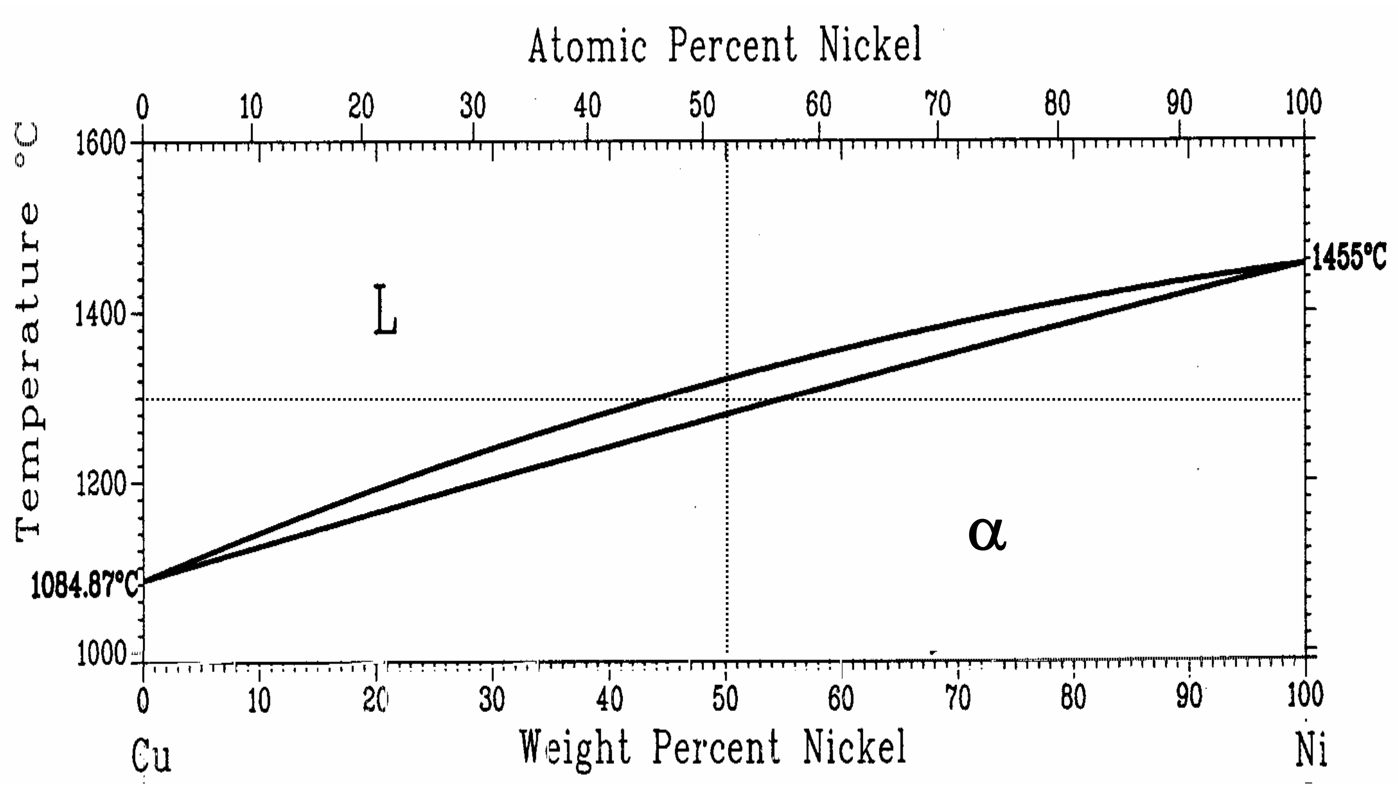
* Qual a composição de carbono de uma liga ferro-carbono para a qual a fração de ferrita total a 726°C é 0,94.

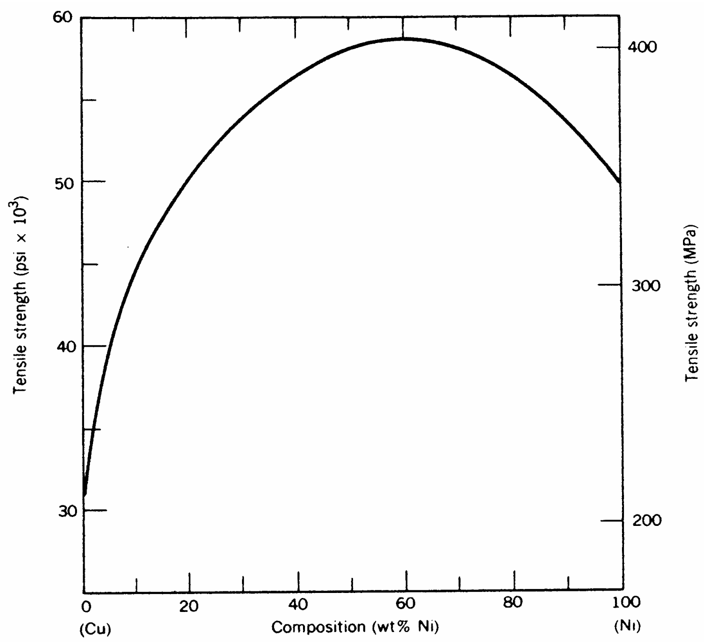
* Geralmente, as propriedades de ligas multifásicas podem ser aproximadas pela relação

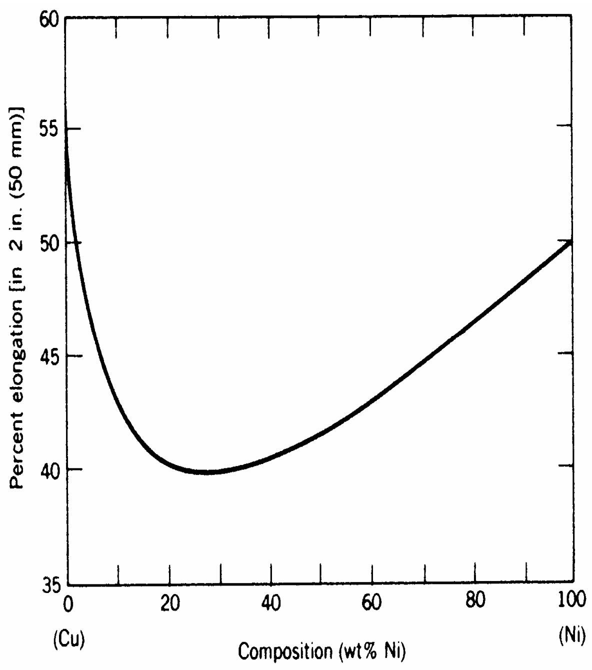
$$E(\text{liga}) = E_{\alpha}V_{\alpha} + E_{\beta}V_{\beta}$$

onde E representa uma propriedade específica (dureza, módulo de elasticidade, etc.), e V é a fração volumétrica. Os índices α e β designam as fases ou microconstituintes existentes. Empregue a relação acima para determinar a dureza Brinell aproximada de uma liga contendo 99,8wt%Fe-0,2wt%C. Assumir os valores de dureza Brinell da ferrita e perlita como sendo 80 e 280 HB respectivamente, e a densidade da ferrita $\rho=7{,}88 g/cm^3$ e da cementita $\rho=7{,}6 g/cm^3$.

* Para uma liga com 99,65%Fe-0,35%C a uma temperatura imediatamente abaixo da temperatura de transformação eutetóide, determine:
a) as frações de cementita e ferrita total,
b) as frações de ferrita primária e perlita,
c) a fração de ferrita eutetóide.



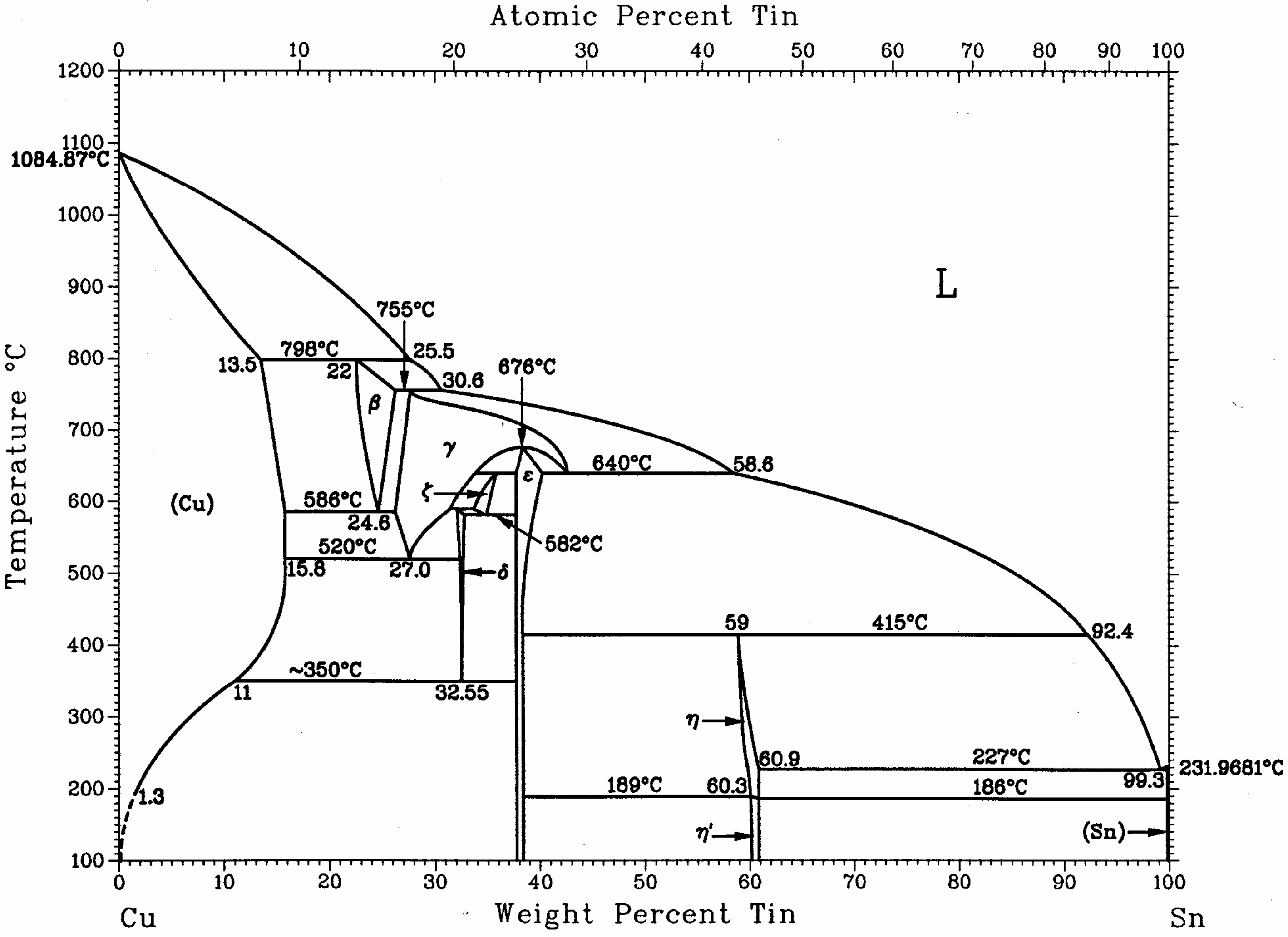




- Quais as fases, suas composições e frações mássicas que estão em equilíbrio a 1300^{o}C em uma liga contendo iguais partes em peso de Cu e Ni? Com o aquecimento em equilíbrio desta liga, de 1000^{o}C a 1600^{o}C, em qual temperatura aparecem os primeiros sinais da fase líquida? Qual a composição deste líquido? em qual temperatura ocorre a fusão total da liga? qual a composição do último sólido presente antes da fusão total da liga?

- Deseja-se produzir uma liga cobre-níquel que tenha um mínimo de resistência à tração (sem deformação a frio) de 380MPa (55000psi) e uma ductilidade de no mínimo 45%EL. É possível produzir tal liga? Se sim, qual deve ser sua composição? Se não, explique o motivo.

Cu-Sn



- * No diagrama Cu-Sn acima estão indicadas somente as regiões monofásicas. Identifique todas as regiões bifásicas e relacione separadamente as transformações trifásicas indicando a reação que ocorre no resfriamento.

- * Quais as fases e frações mássicas presentes a 1000, 800, 600, 355 e 200°C em uma liga contendo 20wt%Sn?

6A - SISTEMAS MONOTÉTICOS BINÁRIOS

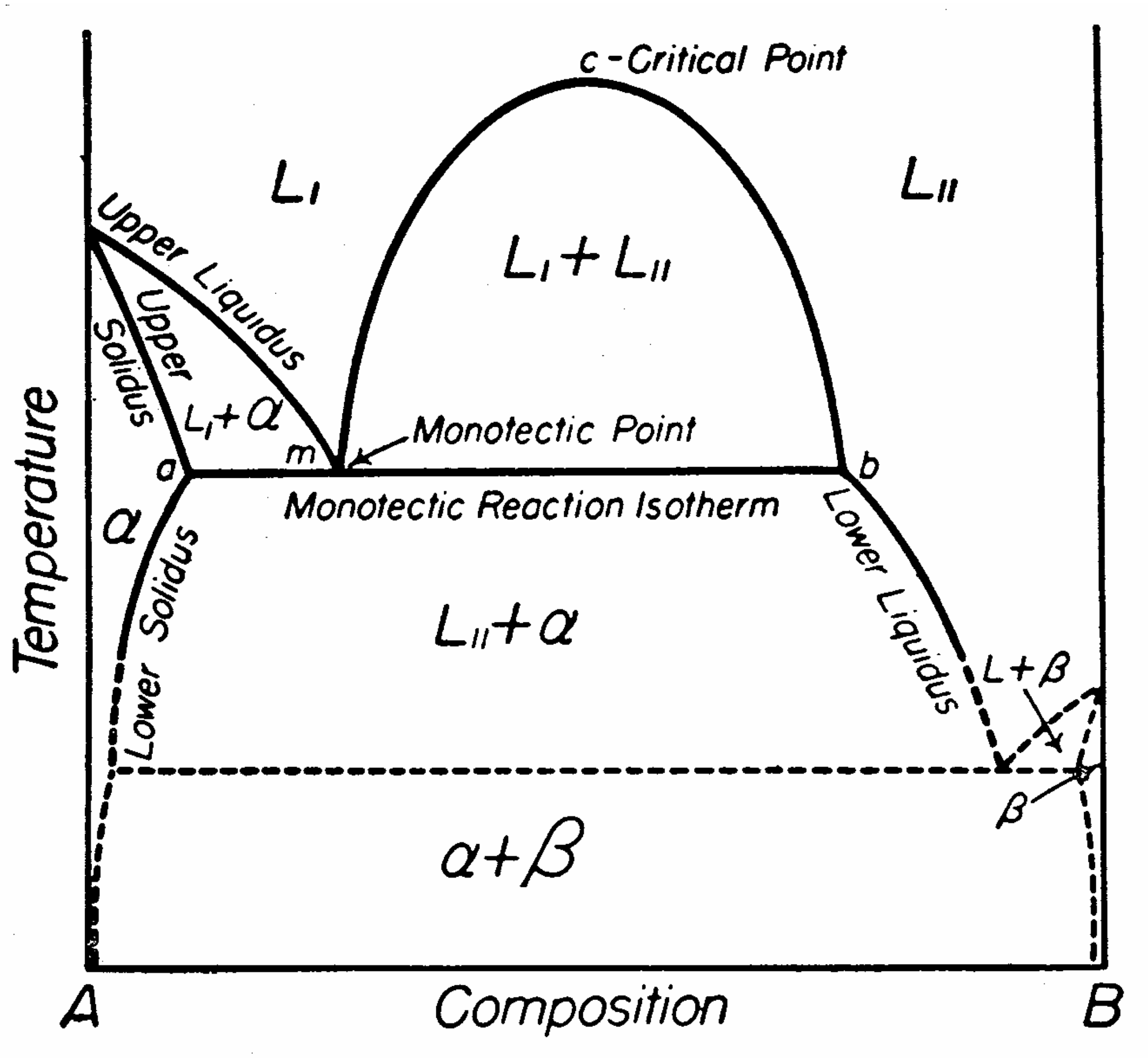


FIG. 6-1

$$\boxed{L_I \underset{\text{aquecimento}}{\overset{\text{resfriamento}}{\rightleftharpoons}} \alpha + L_{II}}$$

6.1 - Ligas de composições monotética, hipo e hipermonotética

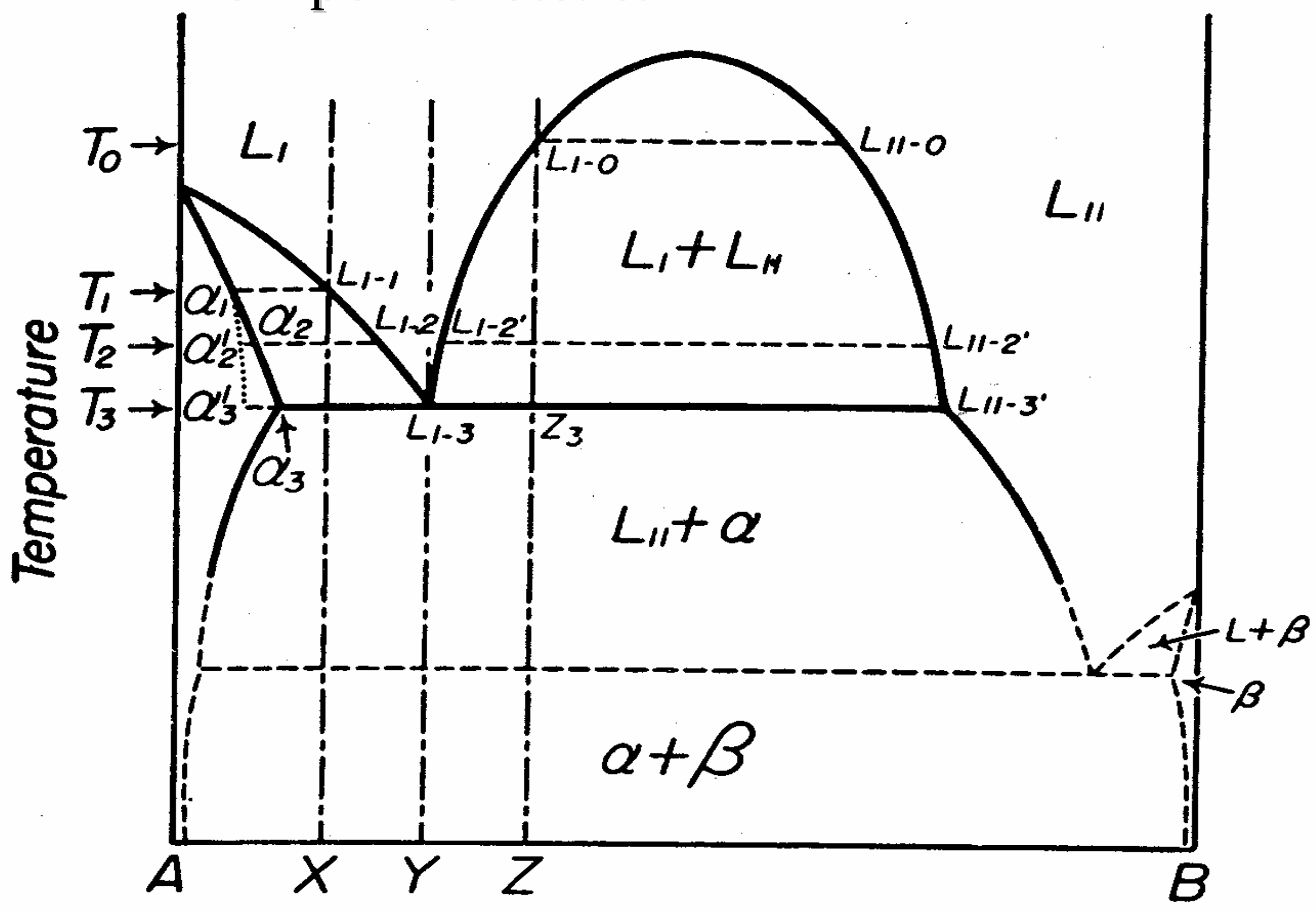


Fig. 6-2

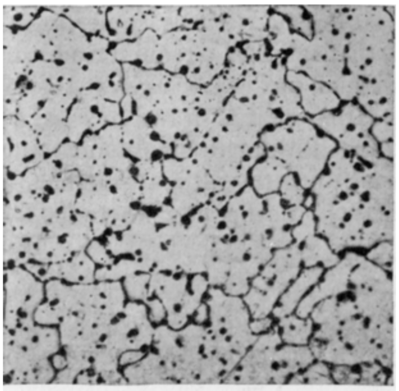


Fig. 6-5. Hypomonotectic Cu + 5% Pb alloy, as cast. Light areas are primary and monotectic Cu; dark areas are Pb which existed as L_{II} at the monotectic temperature. Magnification 100.

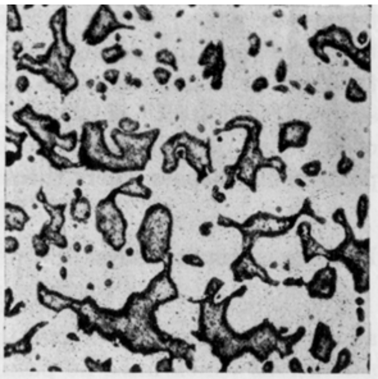


Fig. 6-4. Microstructure of cast monotectic alloy Cu + 36% Pb. Light areas are the Cu-rich matrix of the monotectic constituent; dark areas are the Pb-rich portion, which existed as L_{II} at the monotectic temperature. Magnification 100.

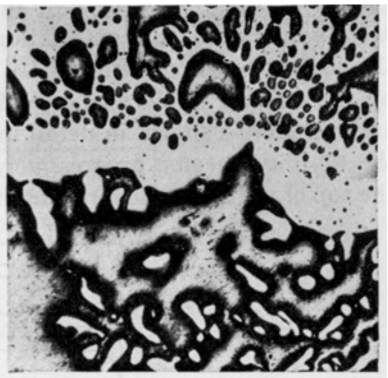
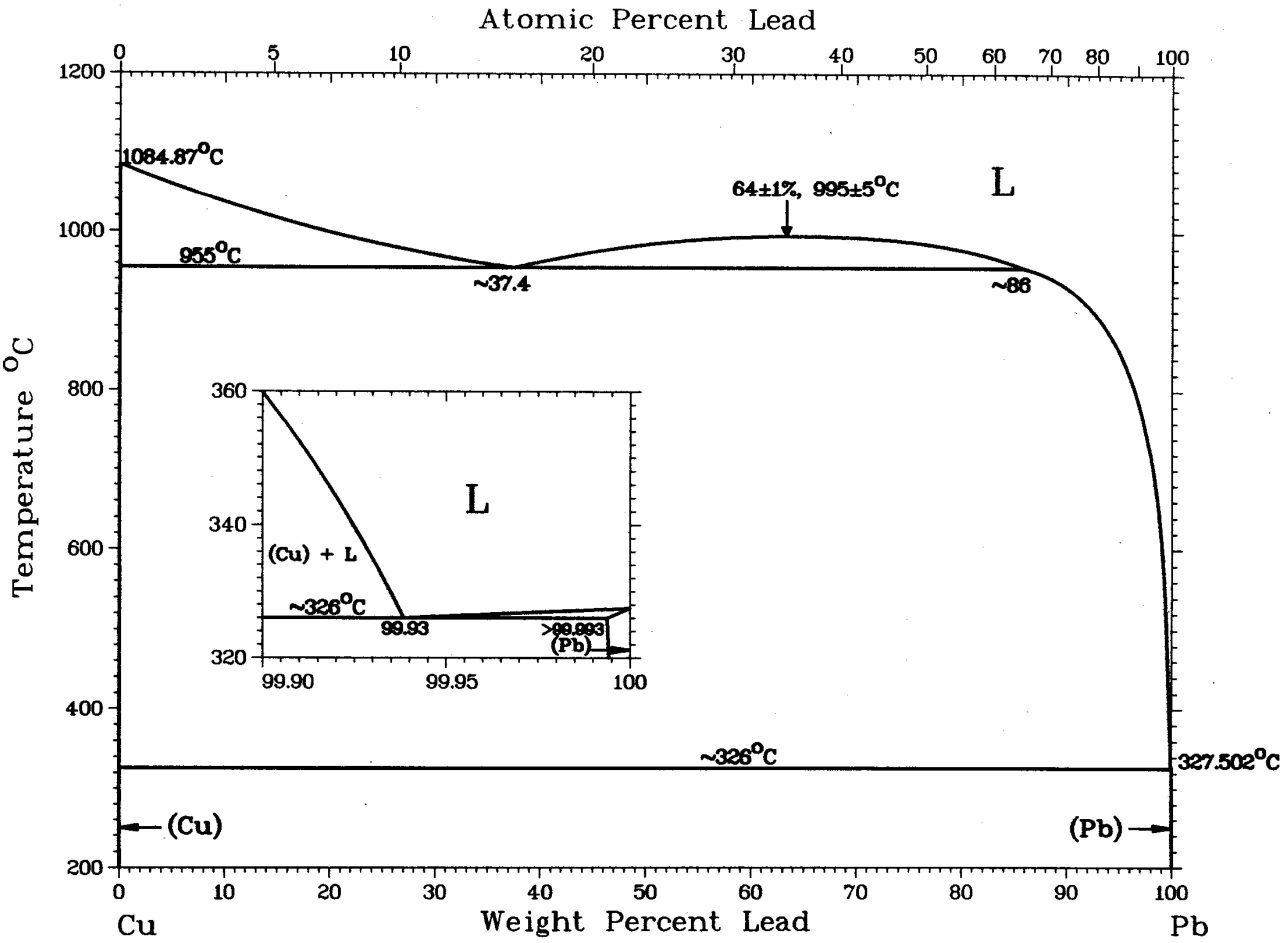
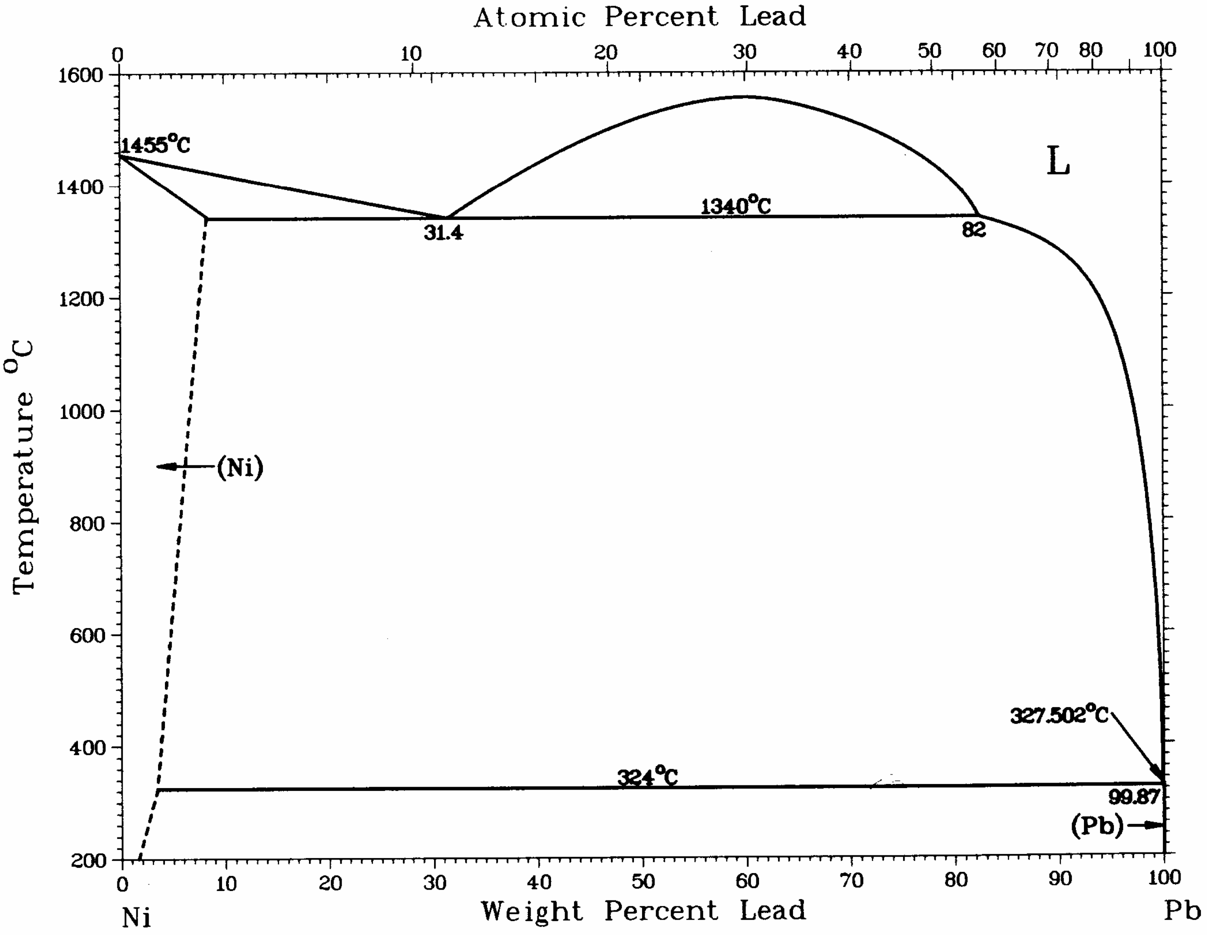


Fig. 6-6. Microstructure at the interface between the two layers in a Cu + 50% Pb hypermonotectic alloy. Upper layer is the product of the monotectic decomposition of L_I (36% Pb); lower layer contains light particles of Cu, precipitated during the cooling of L_{II} from the monotectic temperature down to that of the eutectic, embedded in the dark Pb-rich Pb-Cu eutectic constituent. Magnification 100.

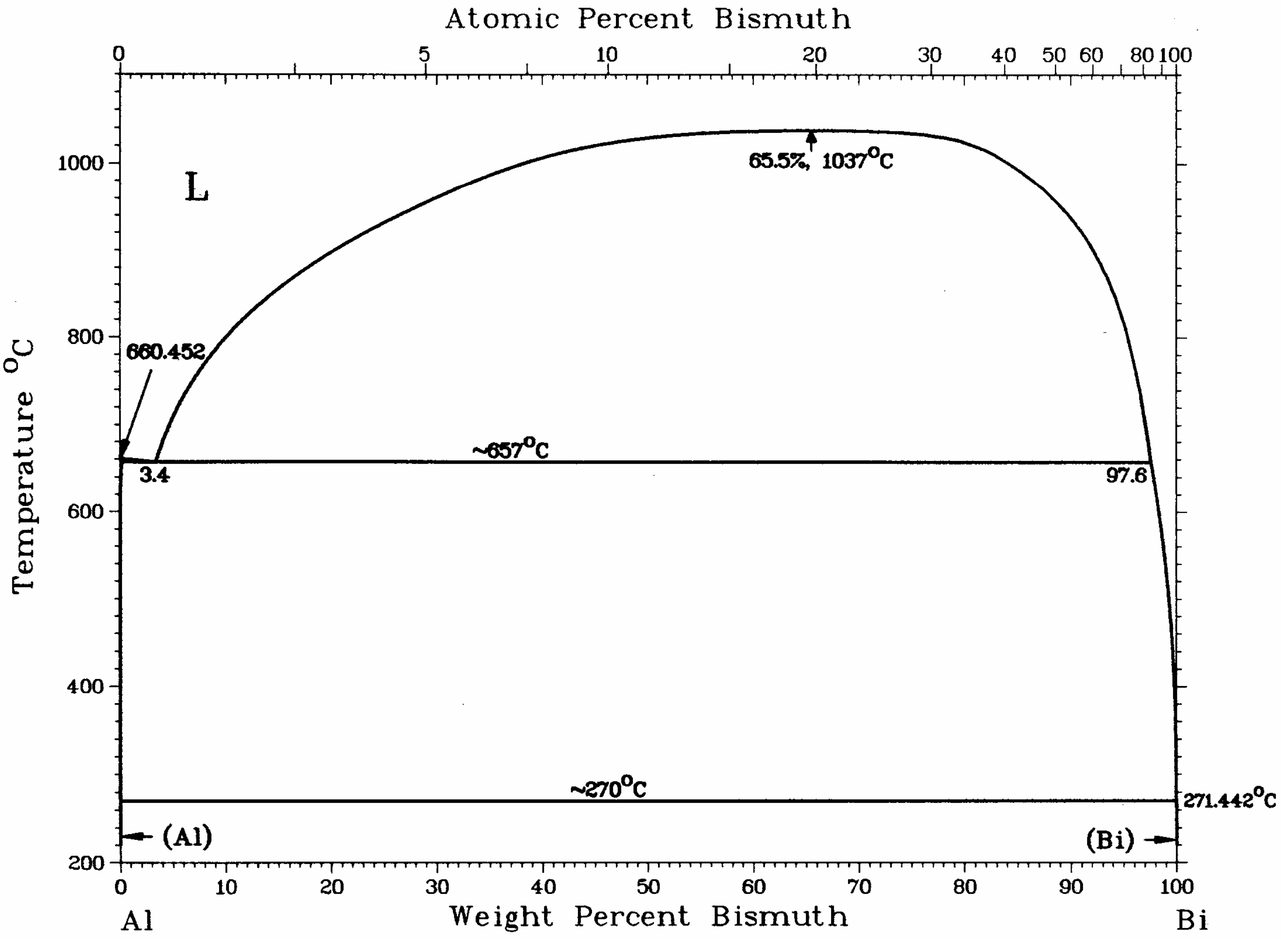
Cu-Pb


Atomic Percent Lead
0
5
10
20
30
40
50
60
70
80
100
1200
1000
800
600
400
200
Temperature °C
1084.87°C
64±1%, 995±5°C
L
955°C
~37.4
~86
360
340
320
L
(Cu) + L
~326°C
99.93
>99.993
(Pb)
99.90
99.95
100
~326°C
327.502°C
(Cu)
(Pb)
0
10
20
30
40
50
60
70
80
90
100
Cu
Weight Percent Lead
Pb

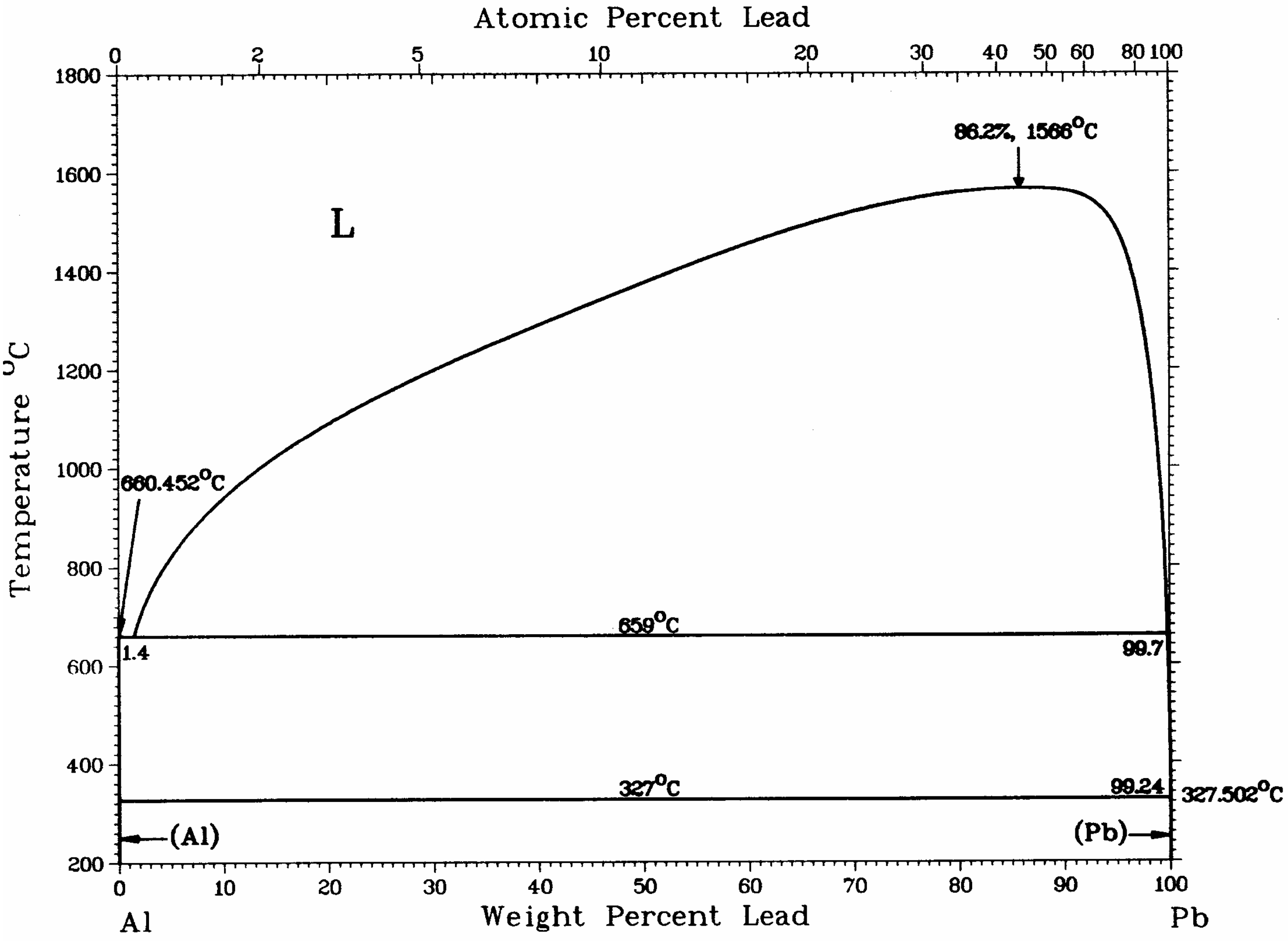
Ni-Pb


Atomic Percent Lead
0
10
20
30
40
50
60
70
80
100
1600
1400
1200
1000
800
600
400
200
Temperature °C
1455°C
L
1340°C
31.4
82
(Ni)
327.502°C
324°C
99.87
(Pb)
0
10
20
30
40
50
60
70
80
90
100
Ni
Weight Percent Lead
Pb

Al-Bi


Atomic Percent Bismuth
0
5
10
20
30
40
50
60
80
100
L
65.5%, 1037°C
660.452
~657°C
3.4
97.6
~270°C
271.442°C
(Al)
(Bi)
Temperature °C
1000
800
600
400
200
0
10
20
30
40
50
60
70
80
90
100
Al
Weight Percent Bismuth
Bi

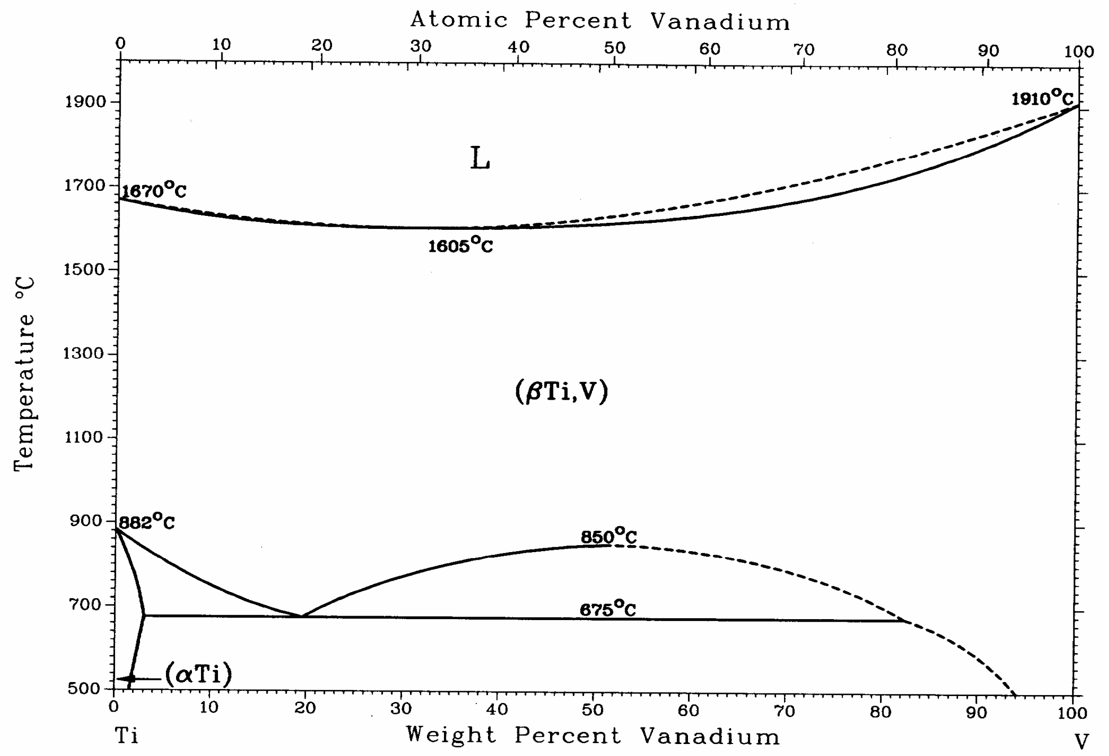
Al-Pb


Atomic Percent Lead
0
2
5
10
20
30
40
50
60
80
100
86.2%, 1566°C
L
660.452°C
659°C
1.4
99.7
327°C
99.24
327.502°C
(Al)
(Pb)
Temperature °C
1800
1600
1400
1200
1000
800
600
400
200
0
10
20
30
40
50
60
70
80
90
100
Al
Weight Percent Lead
Pb

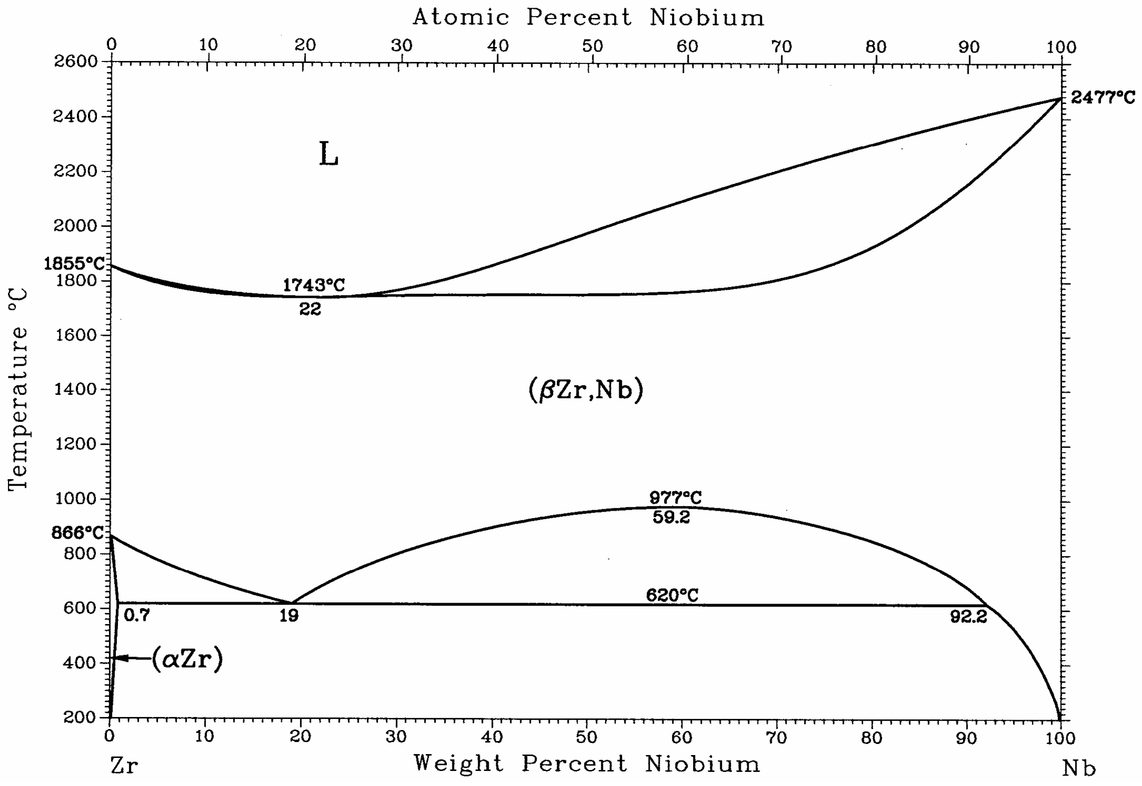
6.B - SISTEMAS MONOTETÓIDES BINÁRIOS

$$\alpha_{I} \underset{\text{aquecimento}}{\overset{\text{resfriamento}}{\rightleftarrows}} \alpha_{II} + \beta$$

Ti-V

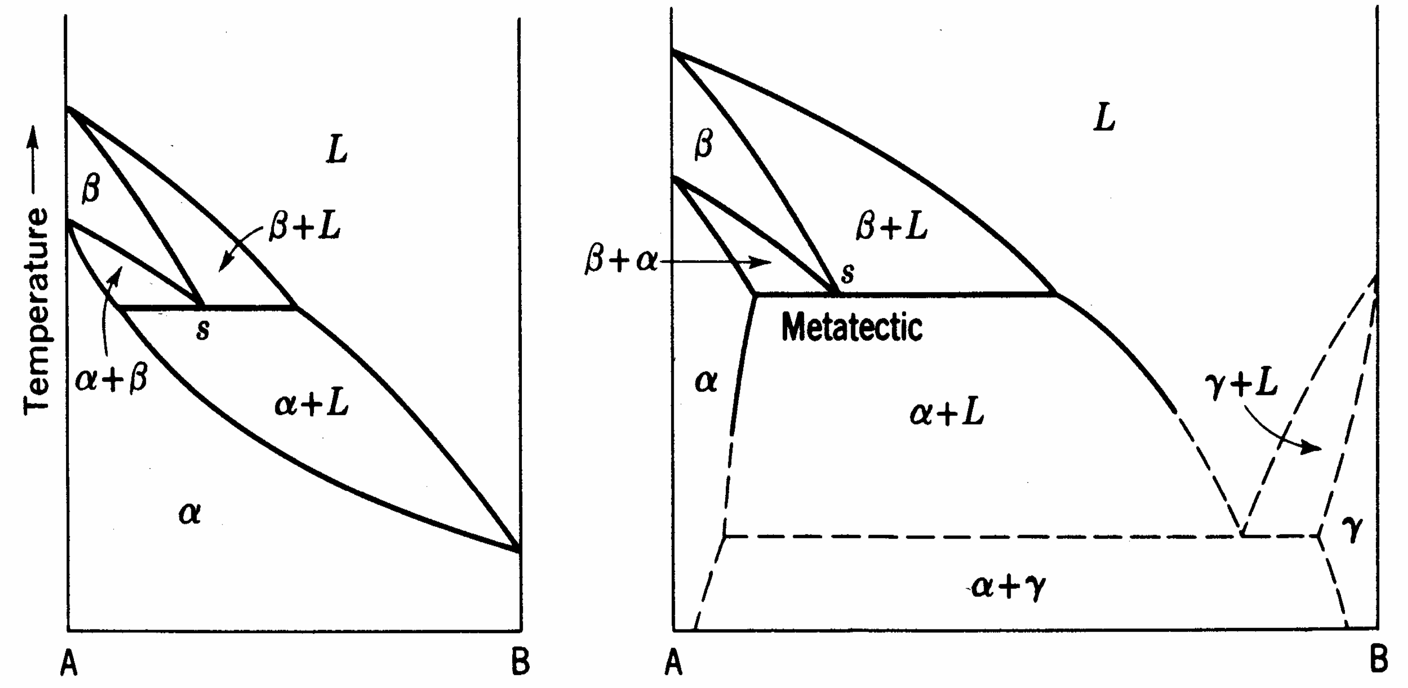


Nb-Zr



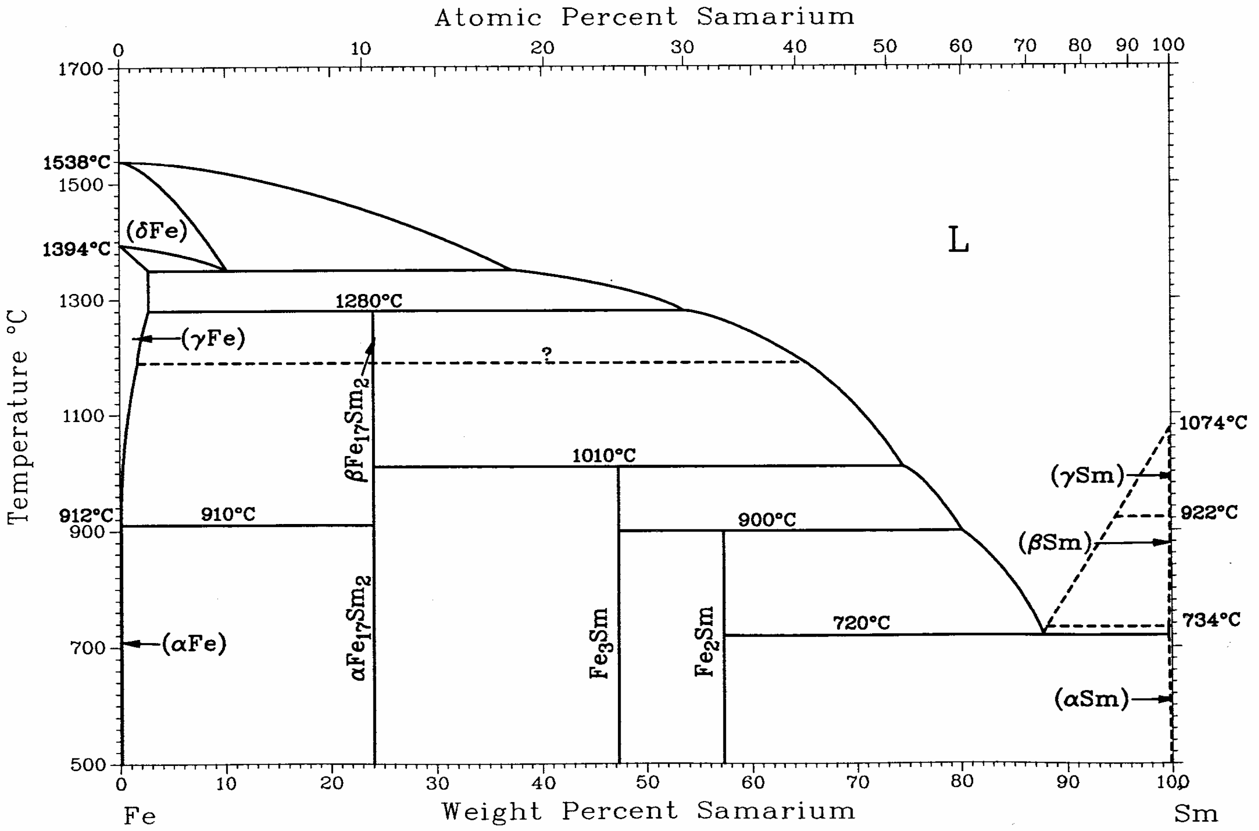
6.C - SISTEMAS METATÉTICOS (catatéticos)

$$\alpha \underset{\text{aquecimento}}{\overset{\text{resfriamento}}{\rightleftharpoons}} \beta + L$$

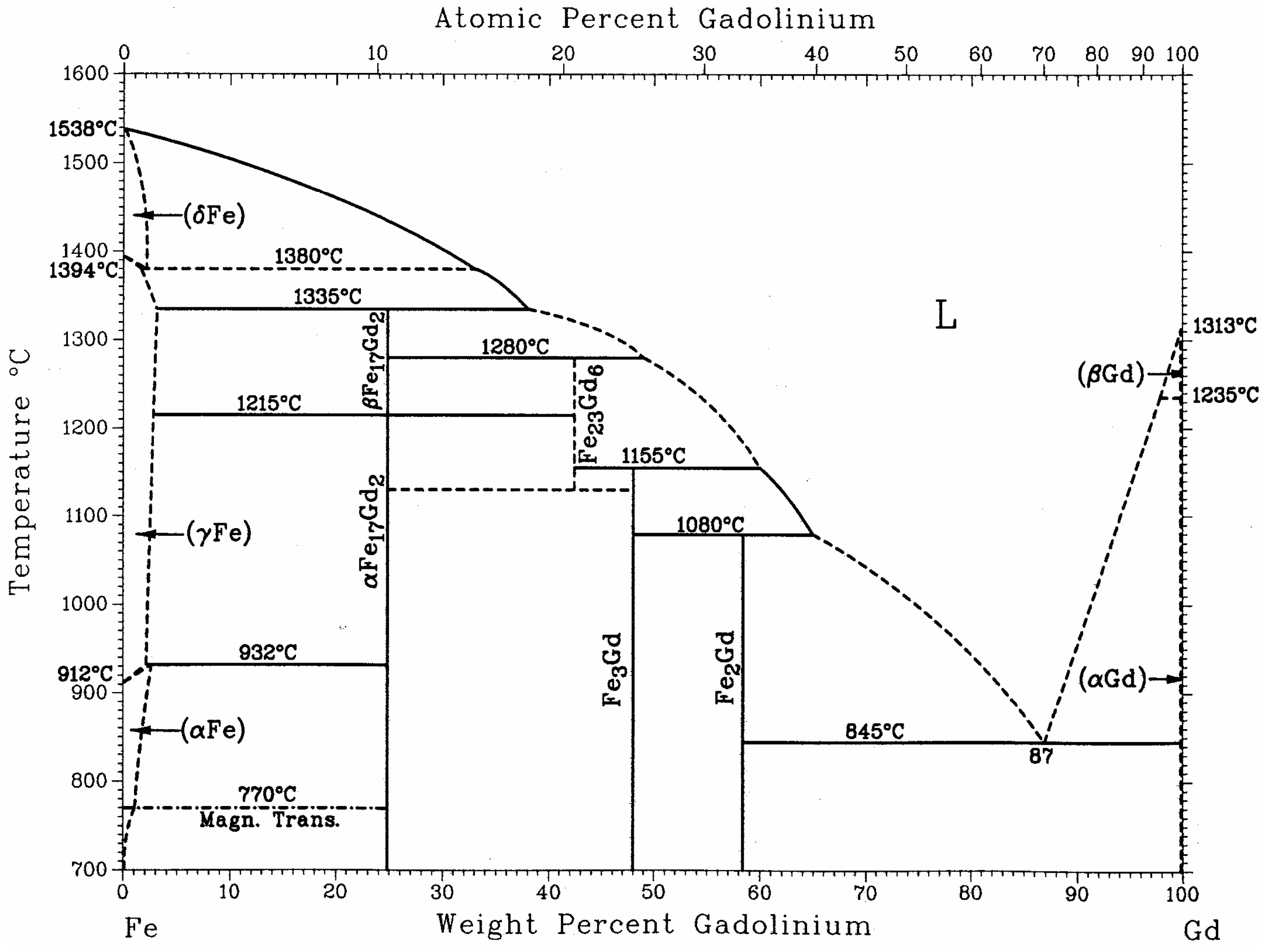


(*c*) Metatectic

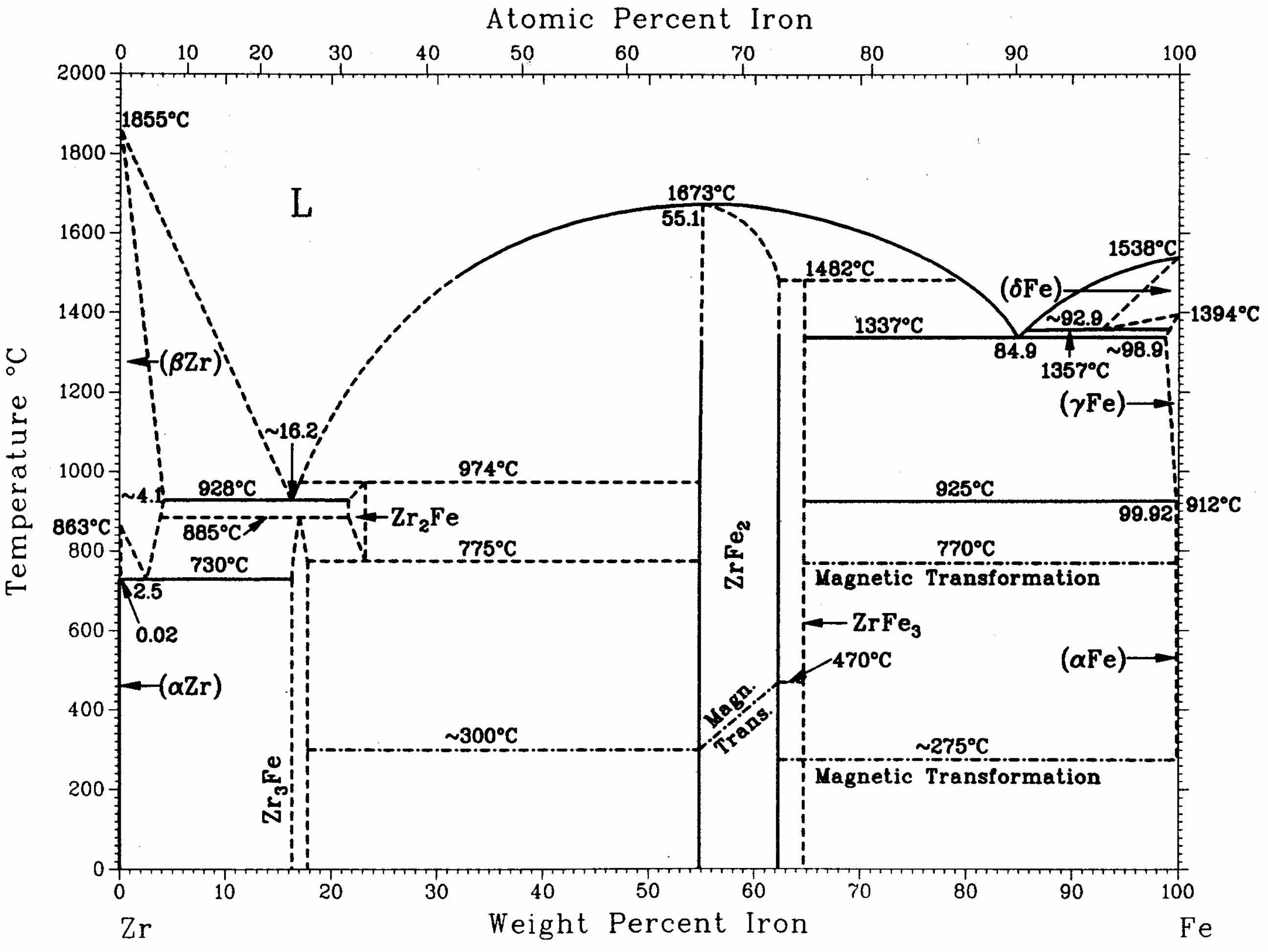
Fe-Sm



Fe-Gd


Atomic Percent Gadolinium
0
10
20
30
40
50
60
70
80
90
100
1600
1500
1400
1300
1200
1100
1000
900
800
700
Temperature °C
1538°C
1394°C
912°C
(δFe)
1380°C
1335°C
L
1313°C
(βGd)
1235°C
$\beta Fe_{17}Gd_2$
1280°C
$Fe_{23}Gd_6$
1215°C
1155°C
(γFe)
$\alpha Fe_{17}Gd_2$
1080°C
Fe_3Gd
Fe_2Gd
932°C
(αGd)
845°C
87
(αFe)
770°C
Magn. Trans.
Weight Percent Gadolinium
Fe
Gd

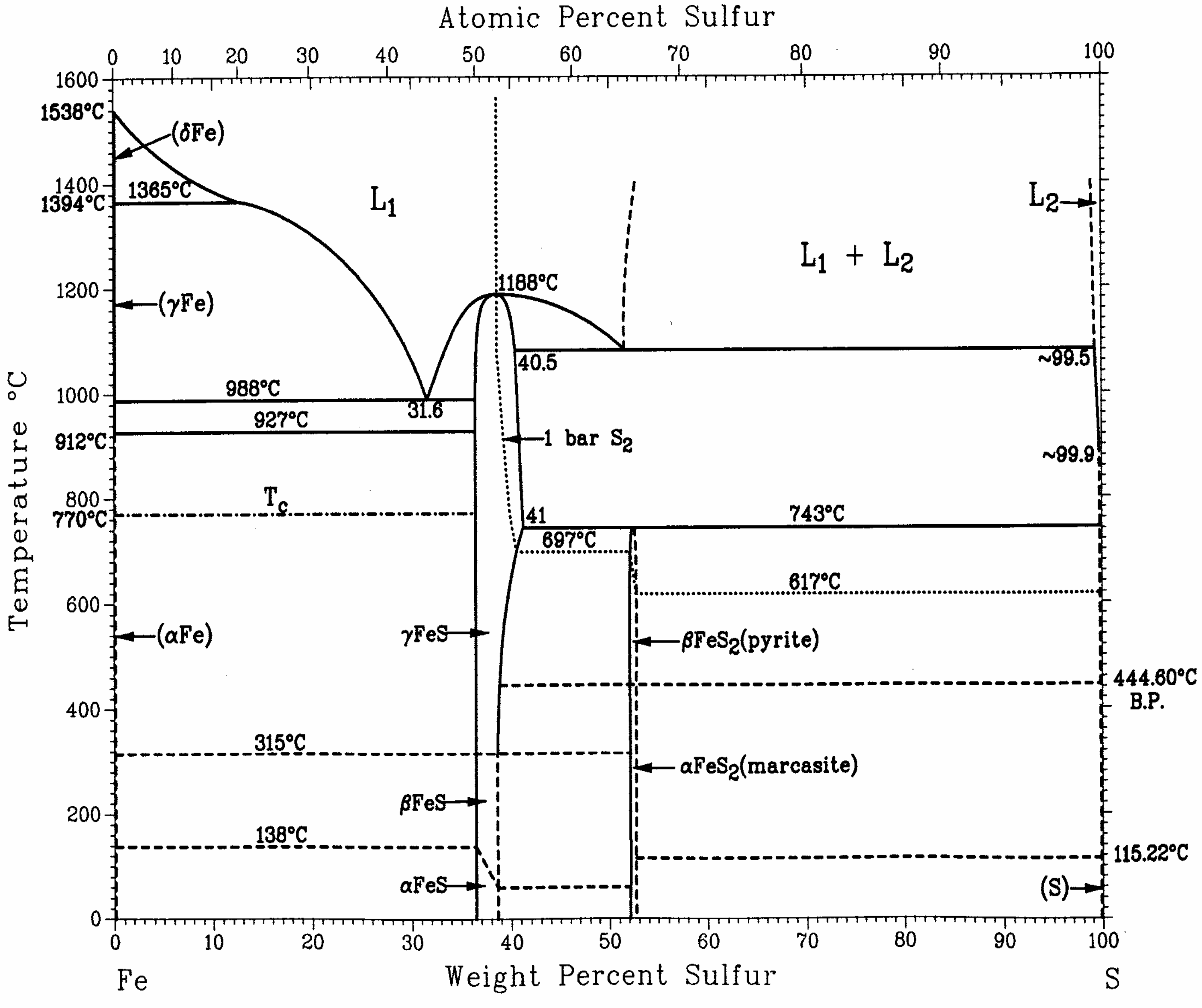
Fe-Zr


Atomic Percent Iron
0
10
20
30
40
50
60
70
80
90
100
2000
1800
1600
1400
1200
1000
800
600
400
200
0
Temperature °C
1855°C
L
1673°C
55.1
1482°C
1538°C
(δFe)
~92.9
1394°C
(βZr)
1337°C
84.9
1357°C
~98.9
(γFe)
~16.2
974°C
~4.1
928°C
925°C
912°C
99.92
863°C
885°C
Zr_2Fe
775°C
770°C
730°C
Magnetic Transformation
2.5
$ZrFe_2$
0.02
$ZrFe_3$
470°C
(αZr)
(αFe)
Magn. Trans.
~300°C
~275°C
Magnetic Transformation
Zr_3Fe
Weight Percent Iron
Zr
Fe

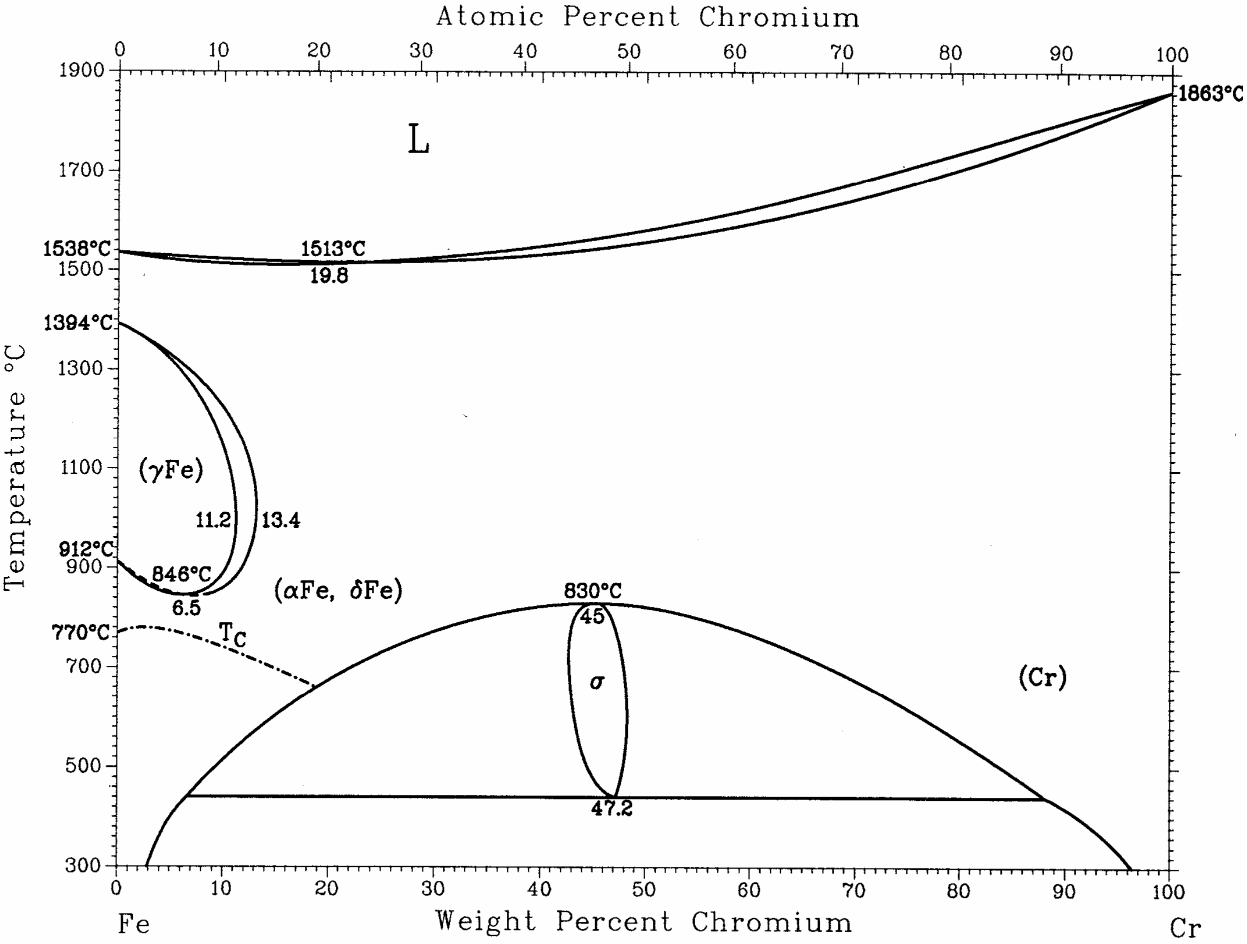
7 - TRANSFORMAÇÕES CONGRUENTES

Uma mudança de fases é denominada congruente quando uma fase se transforma diretamente em outra fase sem que ocorra qualquer alteração na composição durante esta transformação.

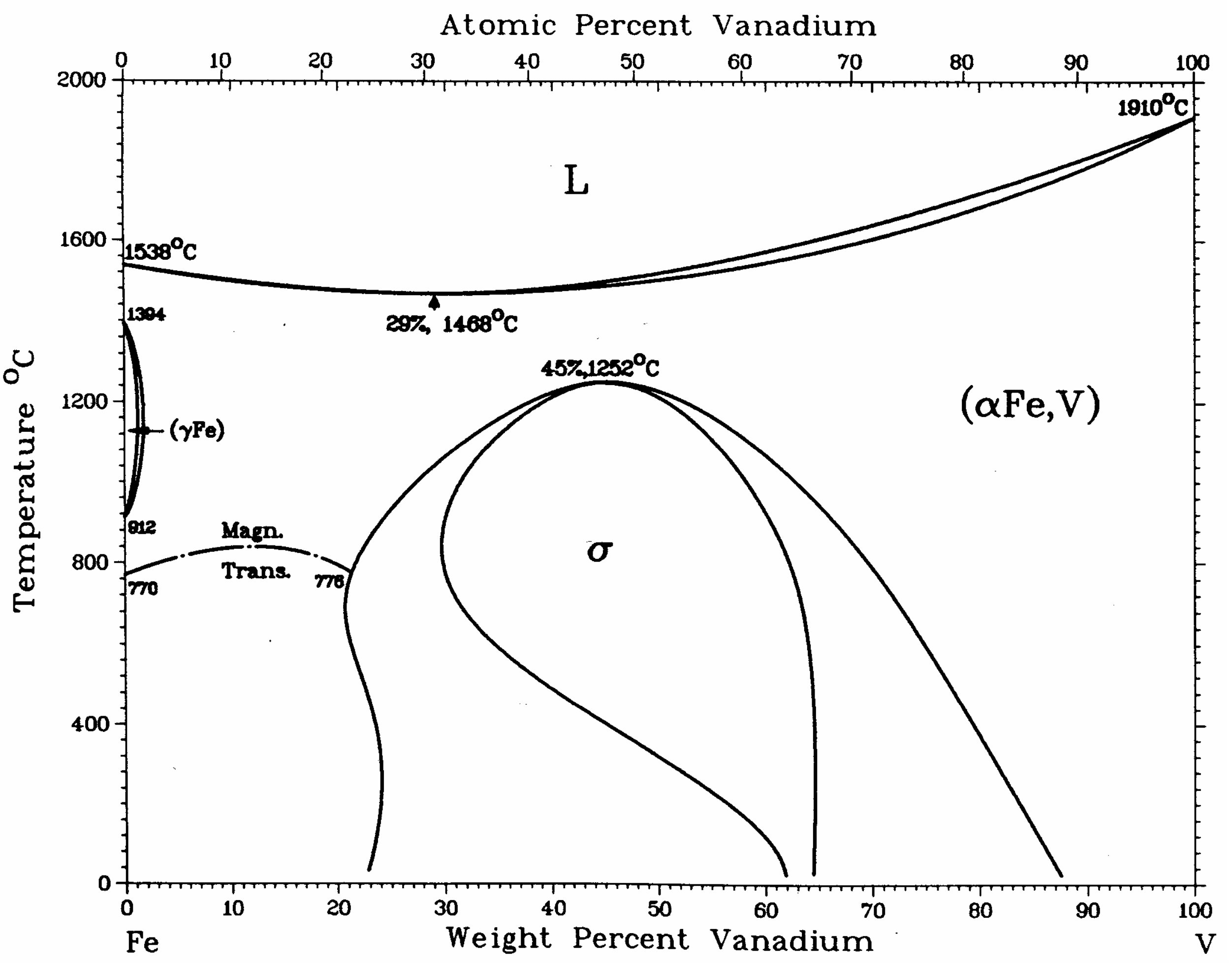
Fe-S



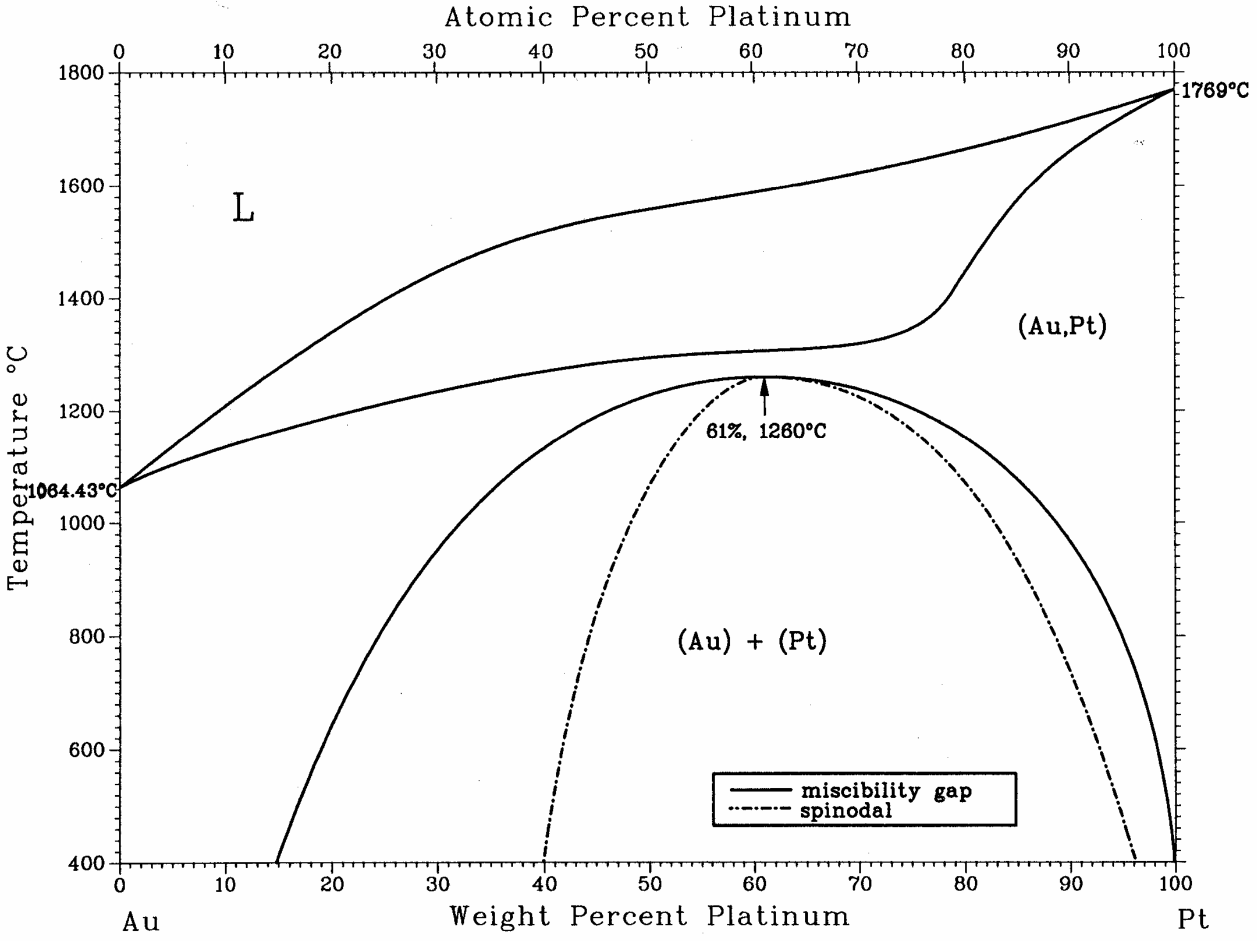
Cr-Fe


Atomic Percent Chromium
0
10
20
30
40
50
60
70
80
90
100
1900
1700
1500
1300
1100
900
700
500
300
Temperature °C
L
1863°C
1538°C
1513°C
19.8
1394°C
(γFe)
11.2
13.4
912°C
846°C
6.5
(αFe, δFe)
770°C
T_C
830°C
45
σ
(Cr)
47.2
0
10
20
30
40
50
60
70
80
90
100
Fe
Weight Percent Chromium
Cr

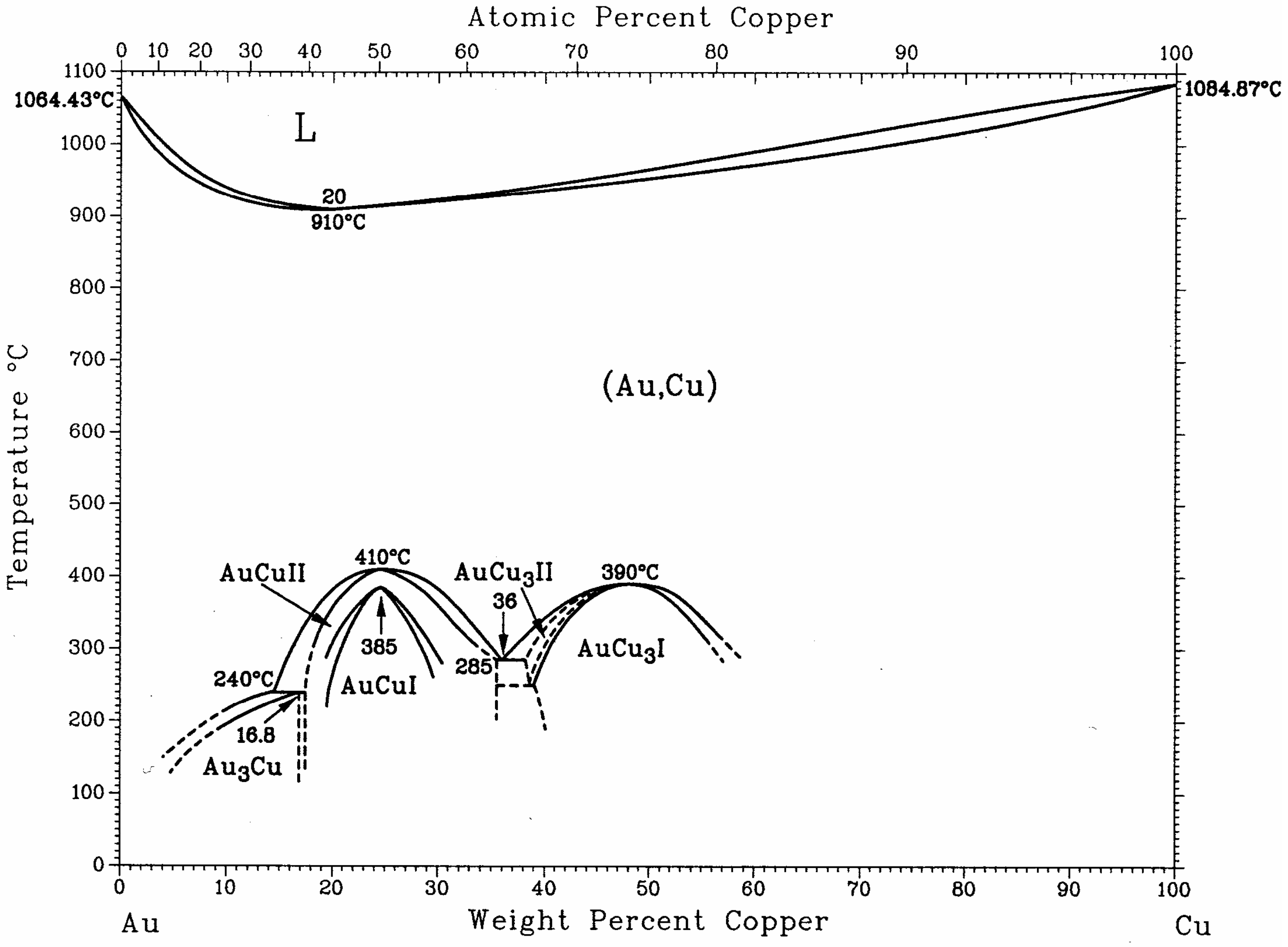
Fe-V


Atomic Percent Vanadium
0
10
20
30
40
50
60
70
80
90
100
2000
1600
1200
800
400
0
Temperature °C
L
1910°C
1538°C
29%, 1468°C
1394
(γFe)
45%,1252°C
(αFe,V)
912
Magn.
Trans.
776
770
σ
0
10
20
30
40
50
60
70
80
90
100
Fe
Weight Percent Vanadium
V

Au-Pt


Atomic Percent Platinum
0
10
20
30
40
50
60
70
80
90
100
1800
1600
1400
1200
1000
800
600
400
Temperature °C
1769°C
L
(Au,Pt)
61%, 1260°C
1064.43°C
(Au) + (Pt)
miscibility gap
spinodal
0
10
20
30
40
50
60
70
80
90
100
Au
Weight Percent Platinum
Pt

Au-Cu


Atomic Percent Copper
0
10
20
30
40
50
60
70
80
90
100
1100
1000
900
800
700
600
500
400
300
200
100
0
Temperature °C
1064.43°C
1084.87°C
L
20
910°C
(Au,Cu)
AuCuII
410°C
AuCu3II
390°C
36
385
285
AuCu3I
240°C
AuCuI
16.8
Au3Cu
0
10
20
30
40
50
60
70
80
90
100
Au
Weight Percent Copper
Cu

8 - SISTEMAS PERITÉTICOS BINÁRIOS

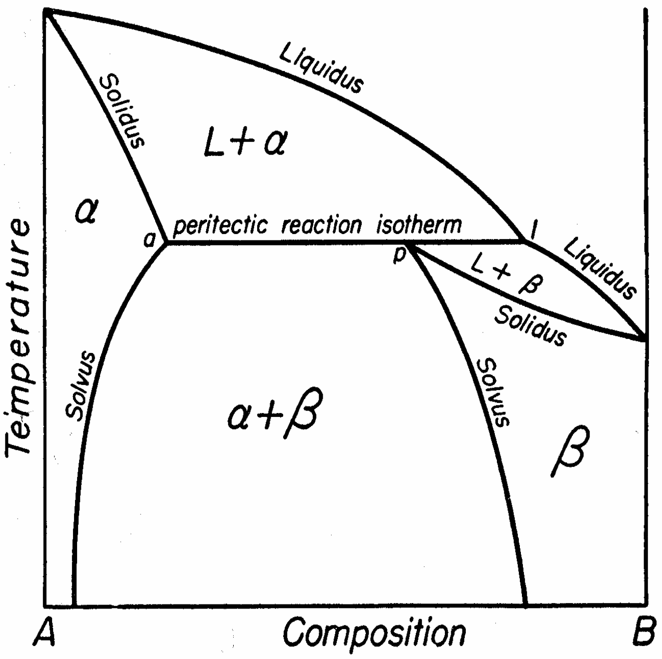


FIG. 8-1

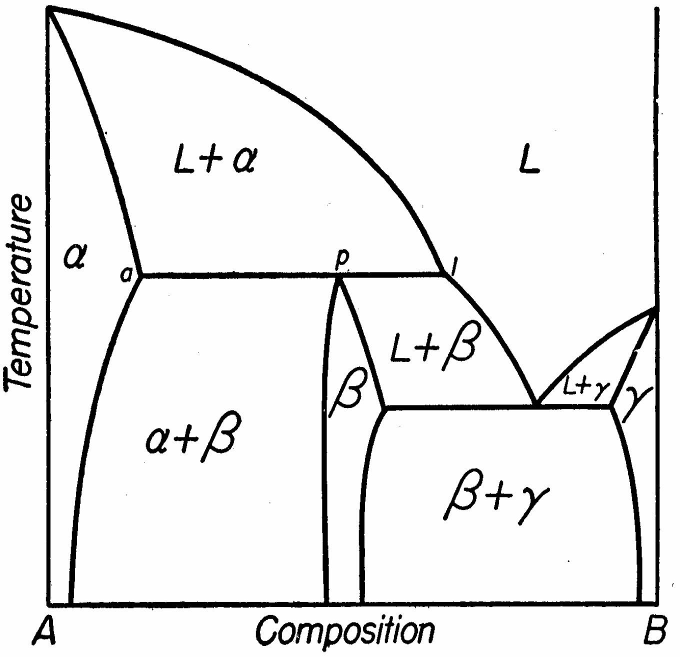
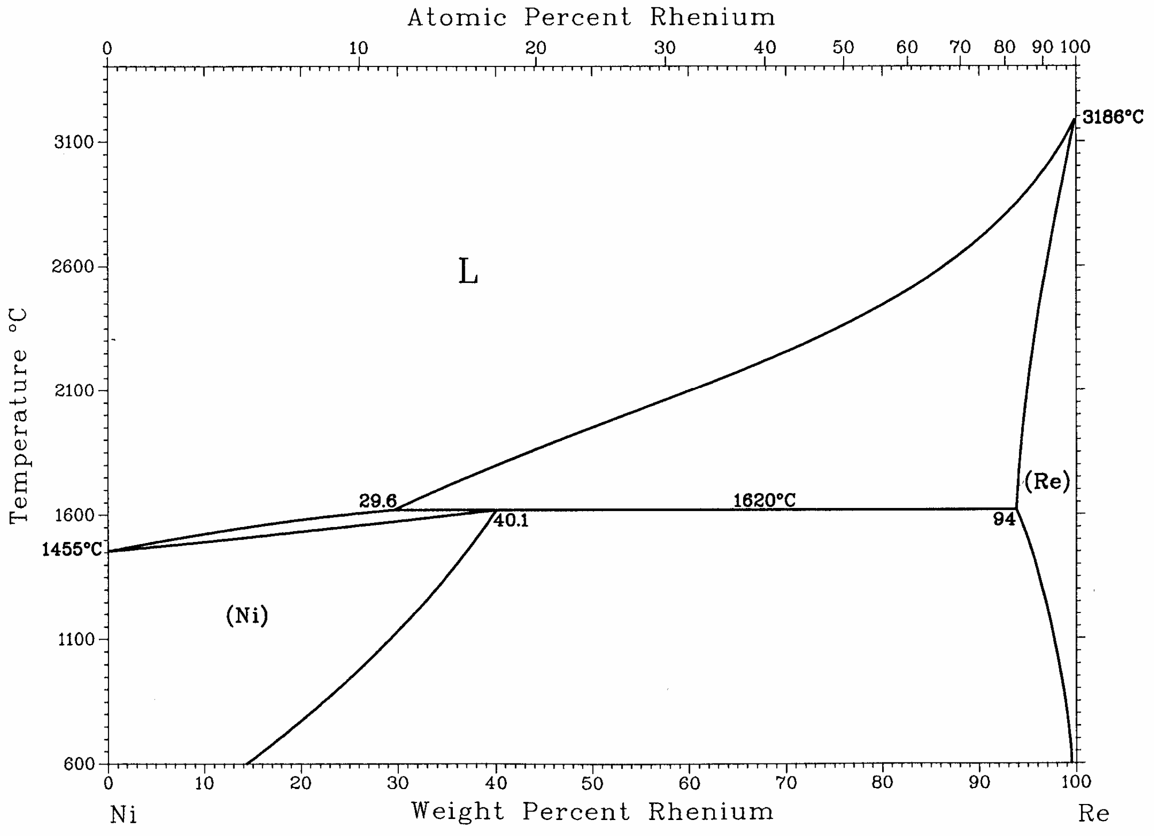


FIG. 8-2

$$\alpha + L \underset{\text{aquecimento}}{\overset{\text{resfriamento}}{\rightleftarrows}} \beta$$

Ni-Re



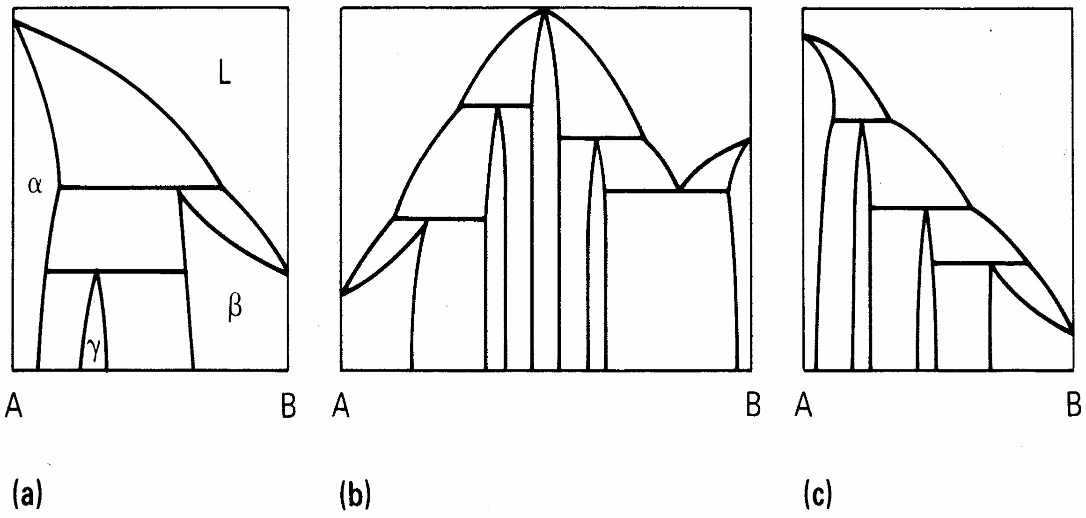
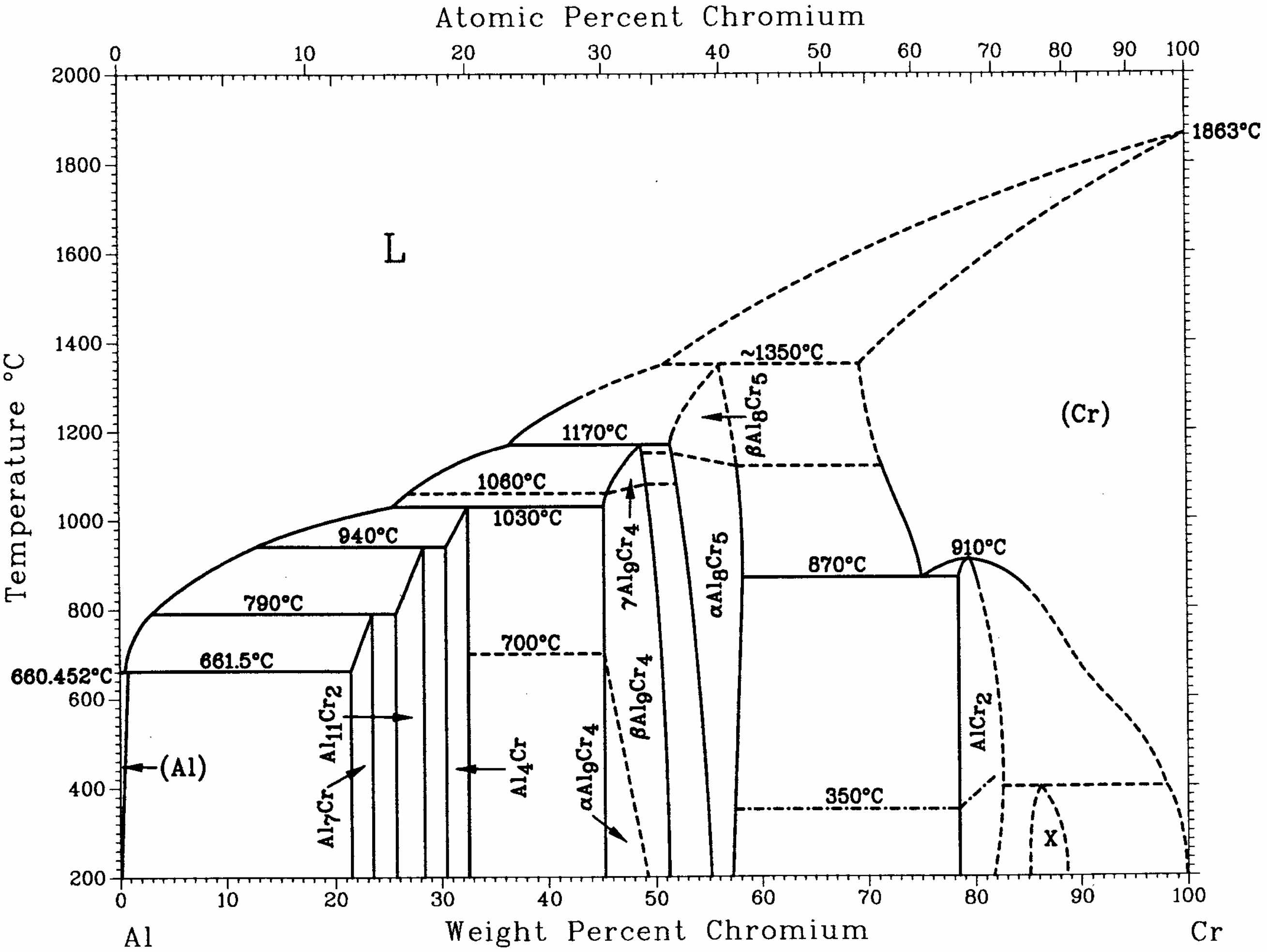


Fig. 1 Typical peritectic phase diagrams. (a) Peritectic reaction α + liquid → β and peritectoid reaction α + β → γ. (b) Peritectic formation of intermetallic phases from a high-melting intermetallic. (c) Peritectic cascade between high- and low-melting components.

Al-Cr



8.1 - Resfriamento em equilíbrio

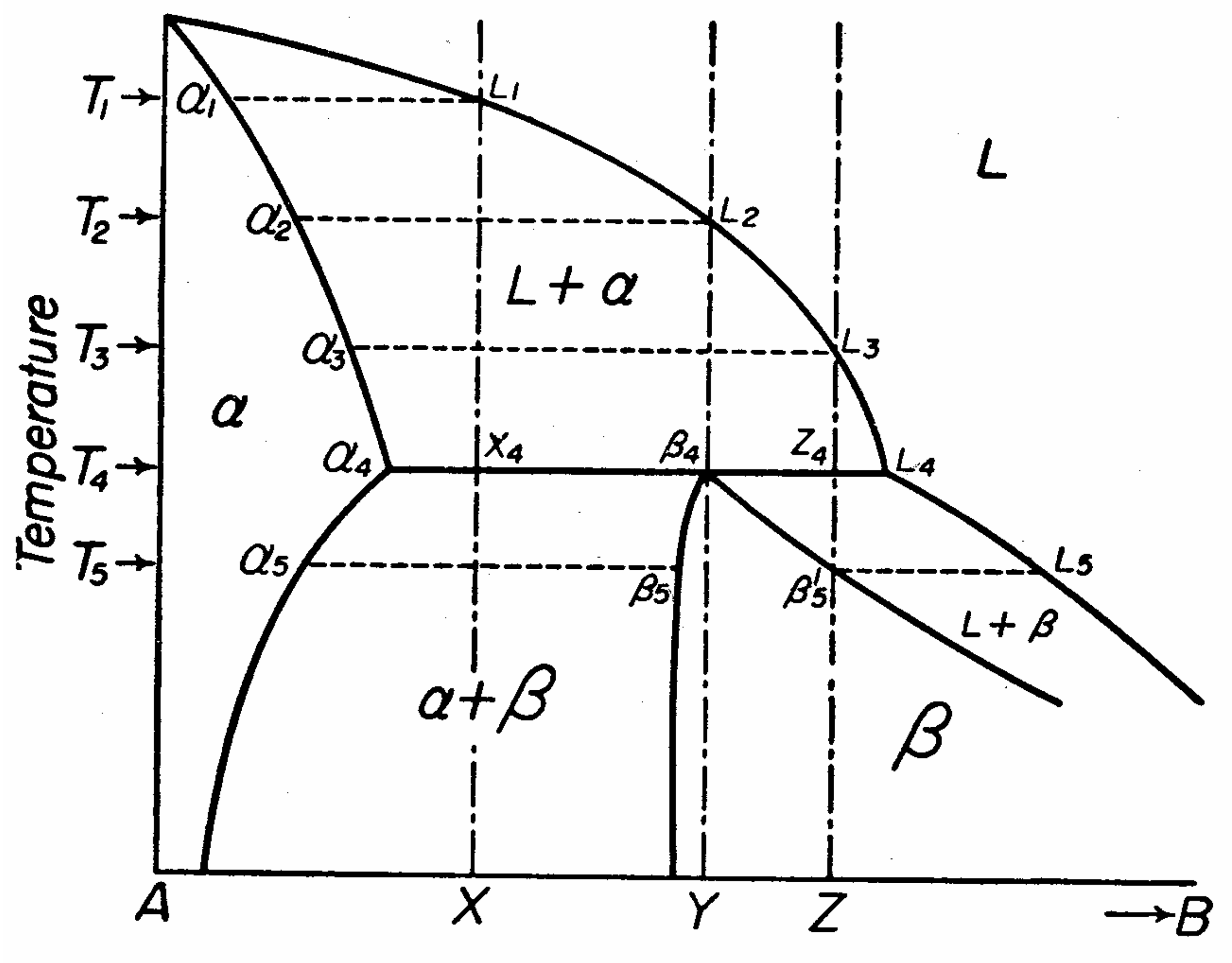


FIG. 8-3

Liga de composição peritética

$$\alpha + L \underset{\text{aquecimento}}{\overset{\text{resfriamento}}{\rightleftharpoons}} \beta$$

$\% \ \alpha_p =$ $\% \ L =$

8.2 - Resfriamento fora de equilíbrio

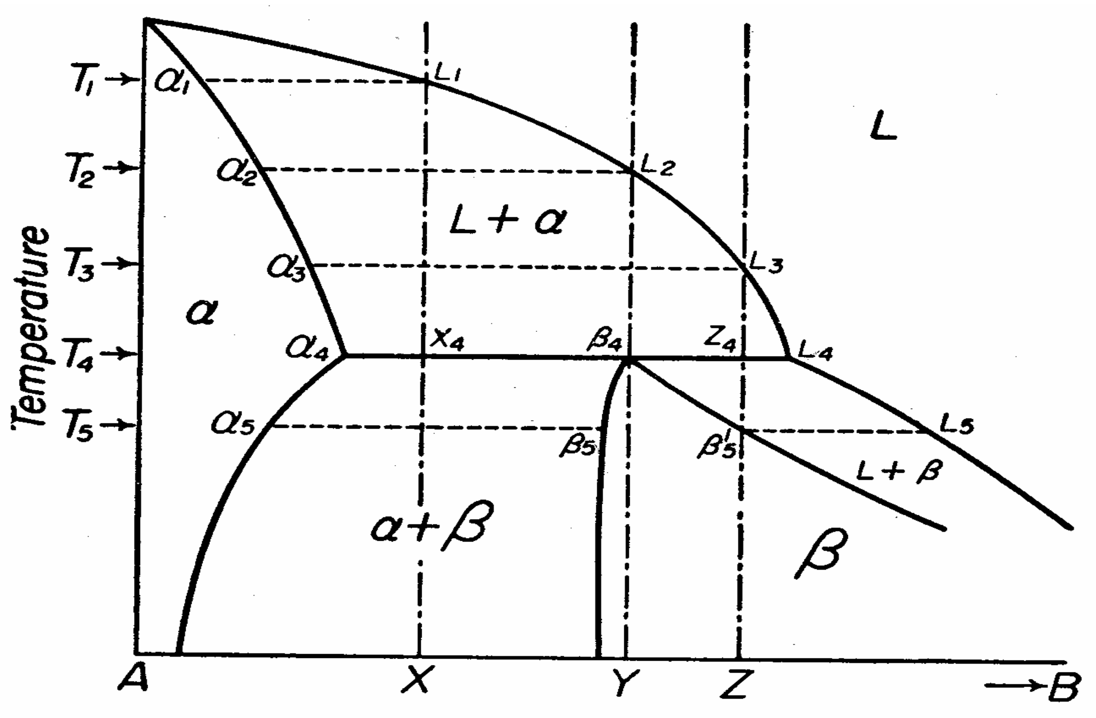
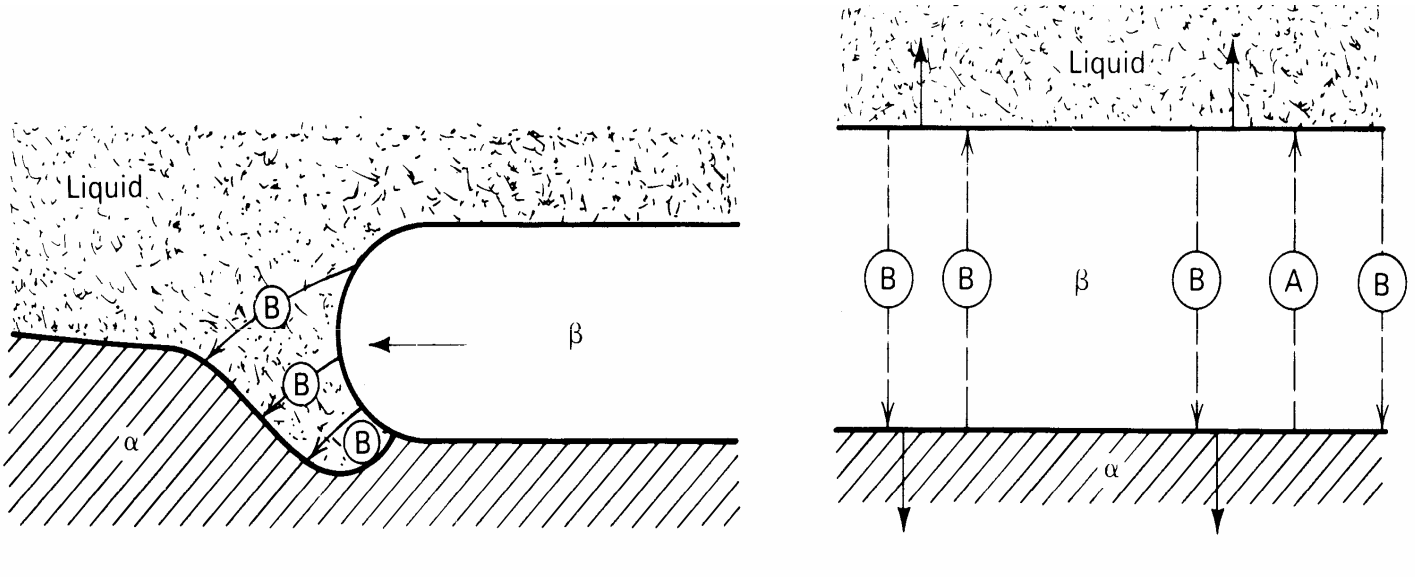


FIG. 8-3

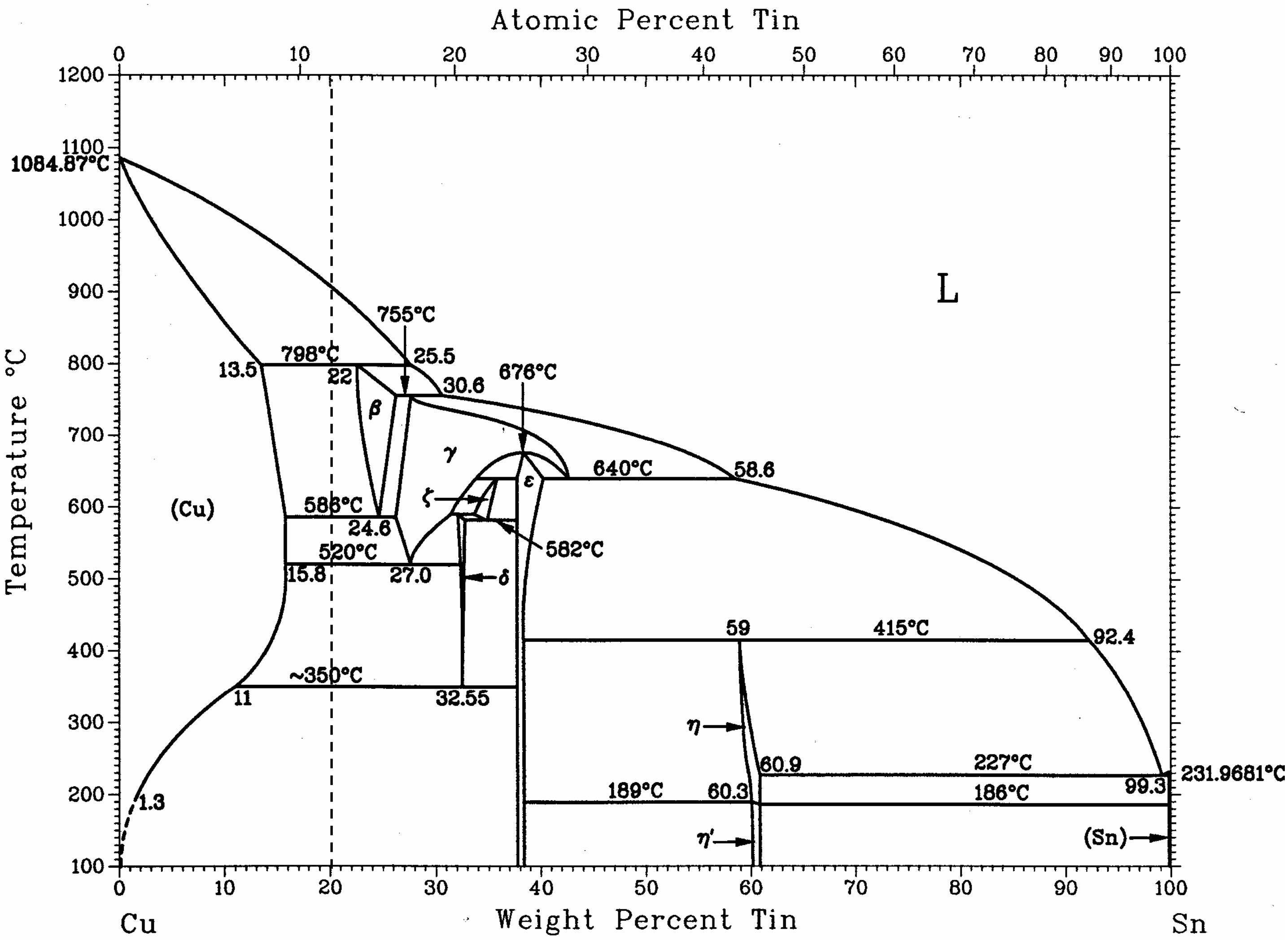


(a)

(b)

Fig. 2 Mechanisms of peritectic reaction and transformation. (a) Lateral growth of a β layer along the α/liquid interface during peritectic reaction by liquid diffusion. (b) Thickening of a β layer by solid-state diffusion during peritectic transformation. The solid arrows indicate growth direction of β; dashed arrows, the diffusion of the atomic species. (Ref 11)

Cu-Sn



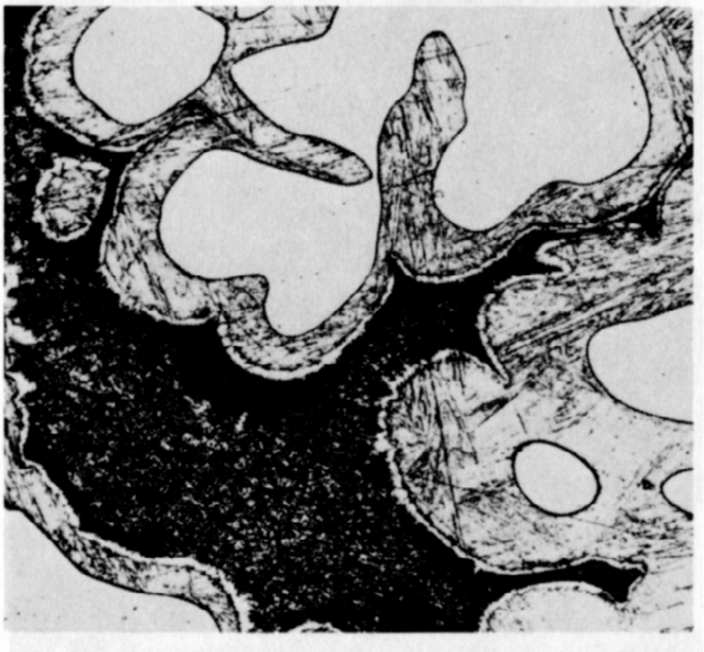


Fig. 9 Start of the peritectic transformation in the same directionally solidified Cu-20Sn alloy shown in Fig. 7, but at higher magnification. Note the homogeneous thickness of the β layers (gray) around the primary α (white). The matrix (dark) is a mixture of tin-rich phases. Mechanically polished, etched in HNO_3. 160×. (Ref 6)

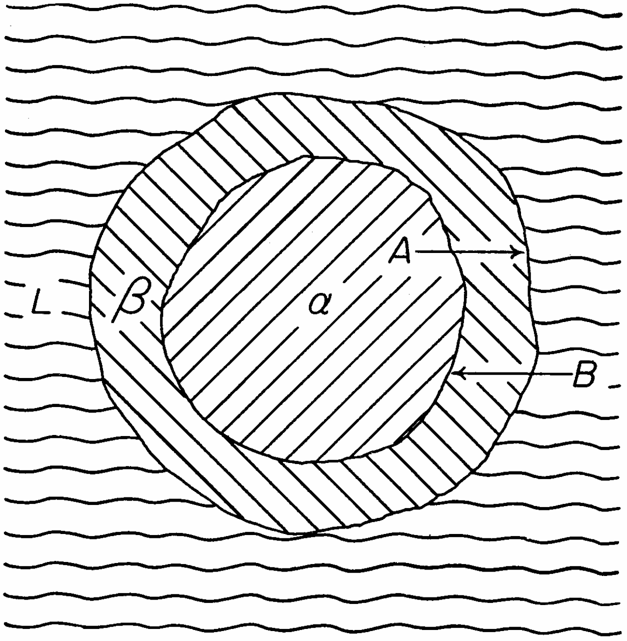
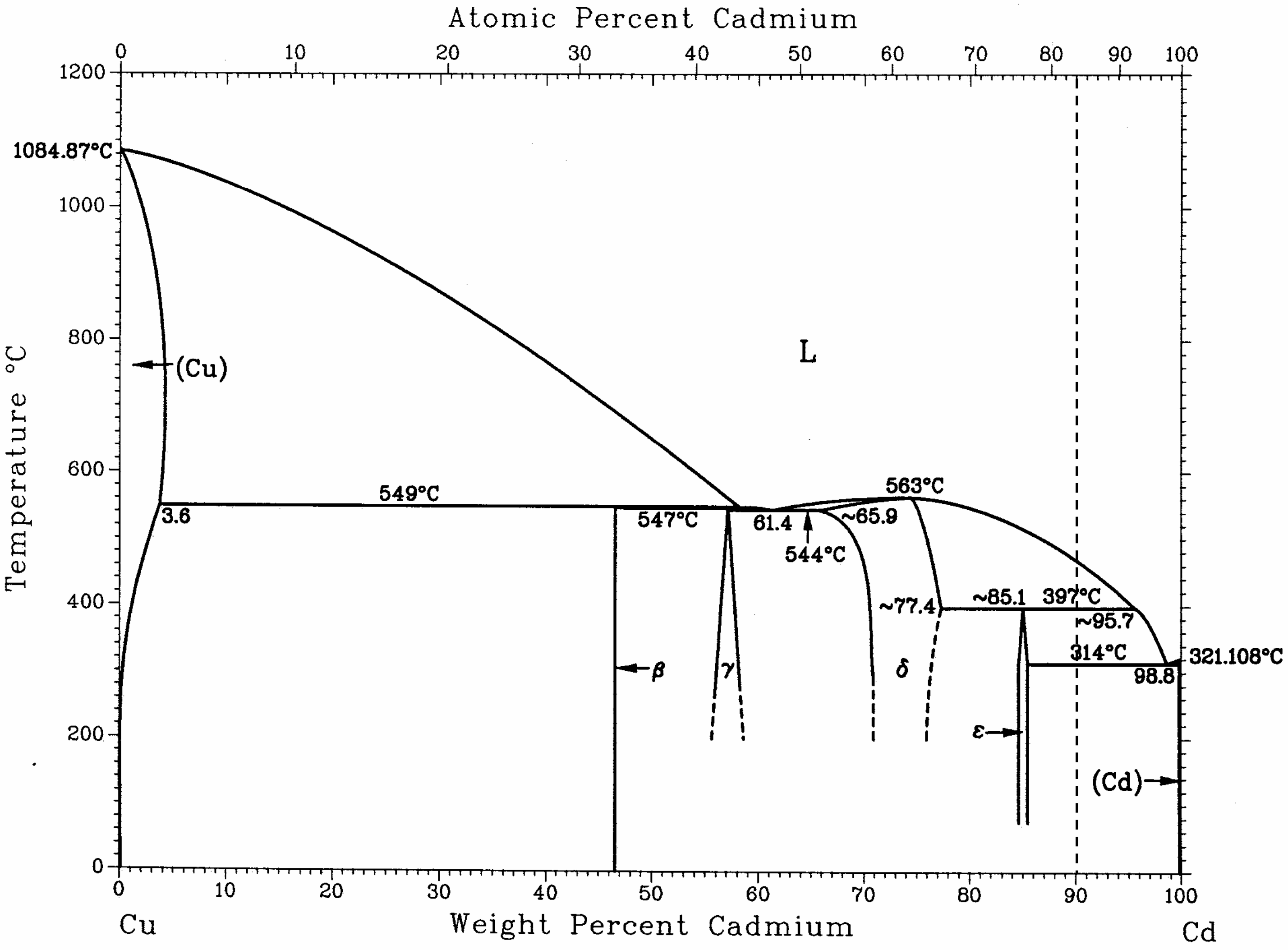


FIG. 8-4. Schematic representation of primary α undergoing peritectic reaction with liquid L to form an envelope of β. The reaction progresses by the diffusion of A atoms outward and B atoms inward through the shell of β.

Cd-Cu



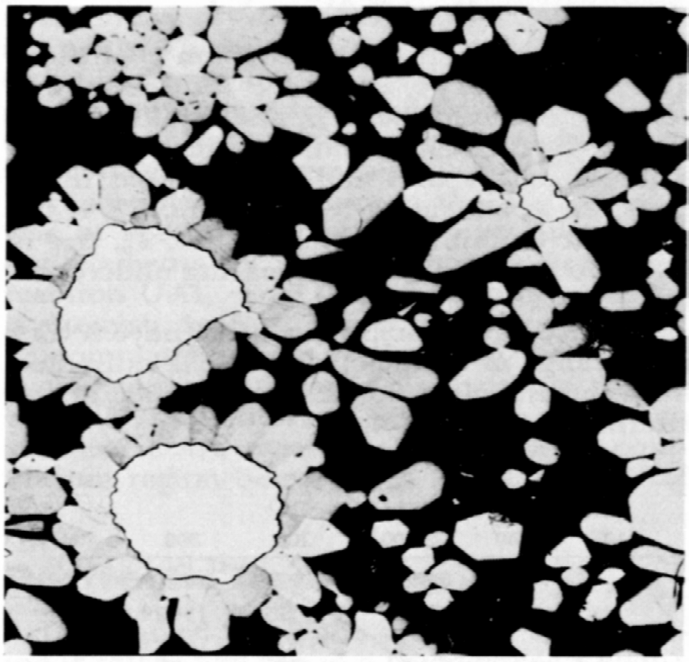


Fig. 15 Microstructure of a Cd-10Cu alloy that was cooled to 410 °C (770 °F) and held 20 h, then cooled to 305 °C (580 °F) and held 160 min (peritectic temperature: 397 °C, or 747 °F). Note the faceted coarse crystals of the peritectically formed $CuCd_3$ envelopes (gray). The primary Cu_5Cd_8 crystals are white; the dark matrix is cadmium. Mechanically polished, etched in HNO_3. 100×

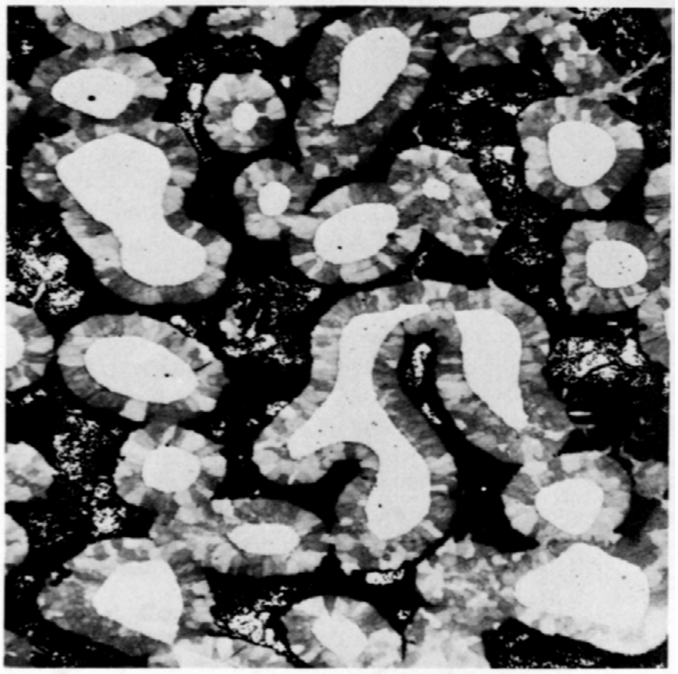
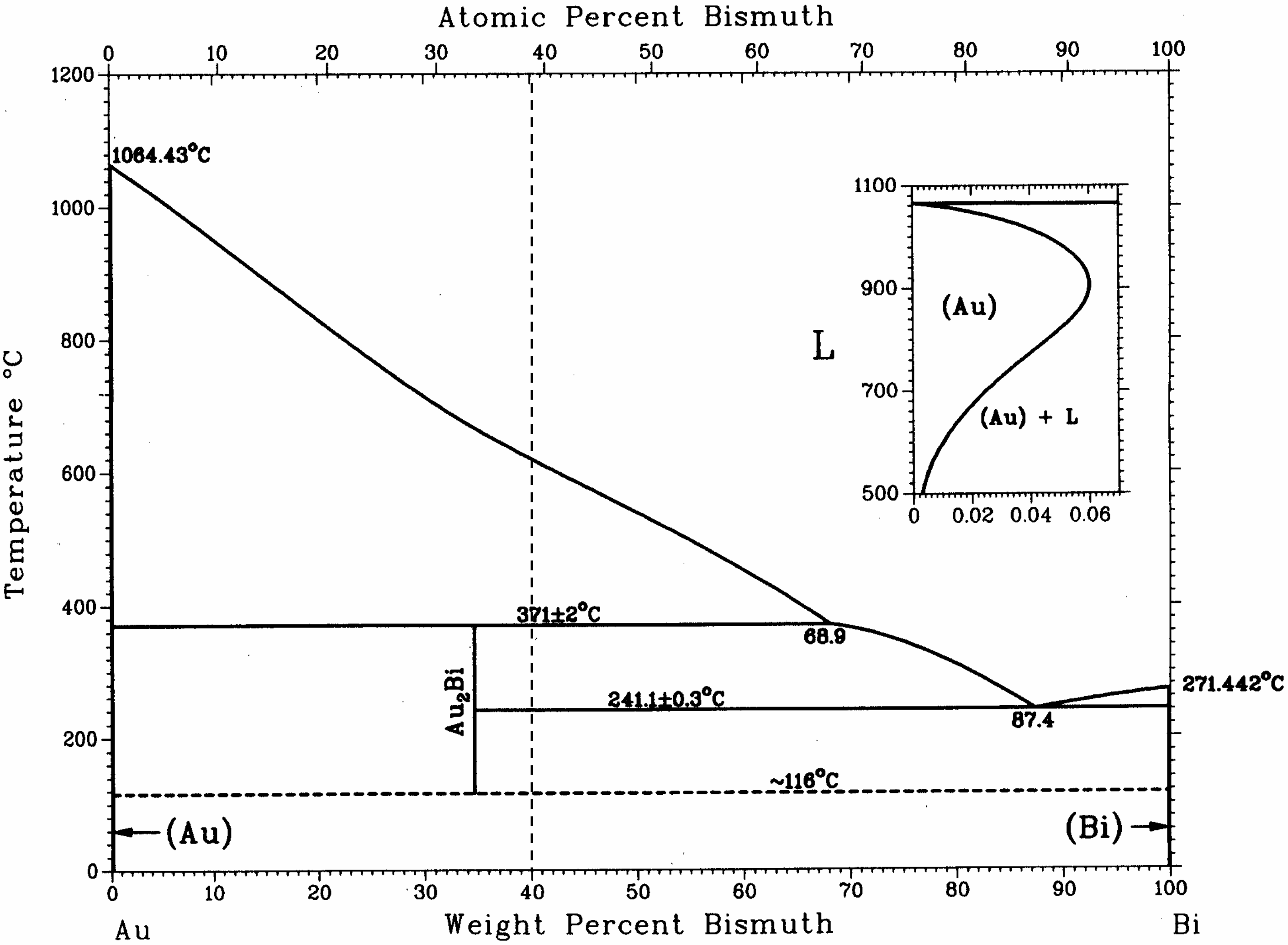


Fig. 16 Same as Fig. 15, except alloy was cooled to 410 °C (770 °F) and held 20 h, then cooled to 275 °C (525 °F) and held 160 min (peritectic temperature: 397 °C, or 747 °F; eutectic temperature: 314 °C, or 597 °F). Note large number of grain boundaries in the peritectic $CuCd_3$ phase (gray) and its smooth interfaces with the primary Cu_5Cd_8 crystals (white) and the matrix Cd (dark). 100×

Au-Bi



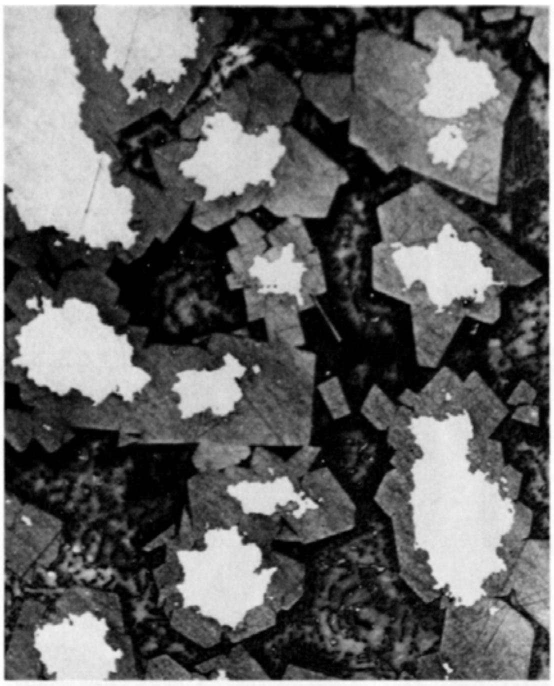


Fig. 18 Peritectic envelope in a Bi-40Au alloy that was cooled to 450 °C (840 °F) and held 5 h, then cooled to 300 °C (570 °F) and held 2 h (peritectic temperature: 373 °C, or 703 °F). The morphology is entirely determined by the anisotropy of the interfacial energy of the face-centered cubic Au_2Bi crystals (gray). The primary crystals are gold (white); the matrix is the Au_2Bi-Bi eutectic. Mechanically polished, contrasted by reactively sputtered interference layer. 200×

Al-U

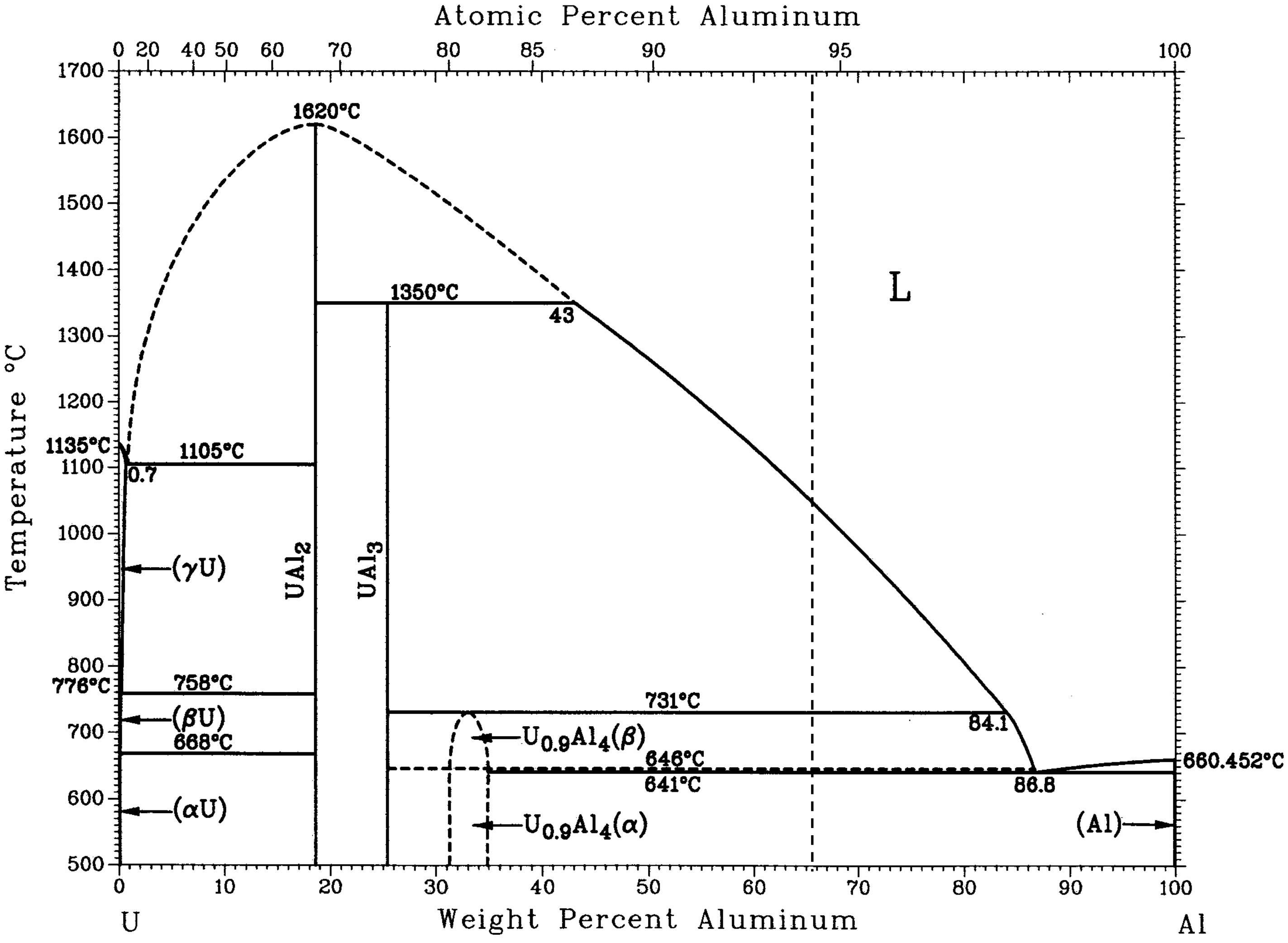


Fig. 3 Primary UAl_3 (gray) partially surrounded by peritectically formed UAl_4 (dark) in an Al-6U alloy that was cooled slowly from above liquidus to 760 °C (1400 °F) and held 10 min, then cooled to 670 °C (1240 °F) and held 15 min (peritectic temperature: 732 °C, or 1350 °F). The matrix is aluminum (white) with UAl_4 (dark) eutectic. This $UAl_3 + Al \rightarrow UAl_4$ reaction leads to unfavorable rolling behavior. Electrolytically polished, etched in 50% HNO_3. 700×

9 - SISTEMAS PERITETÓIDES BINÁRIOS

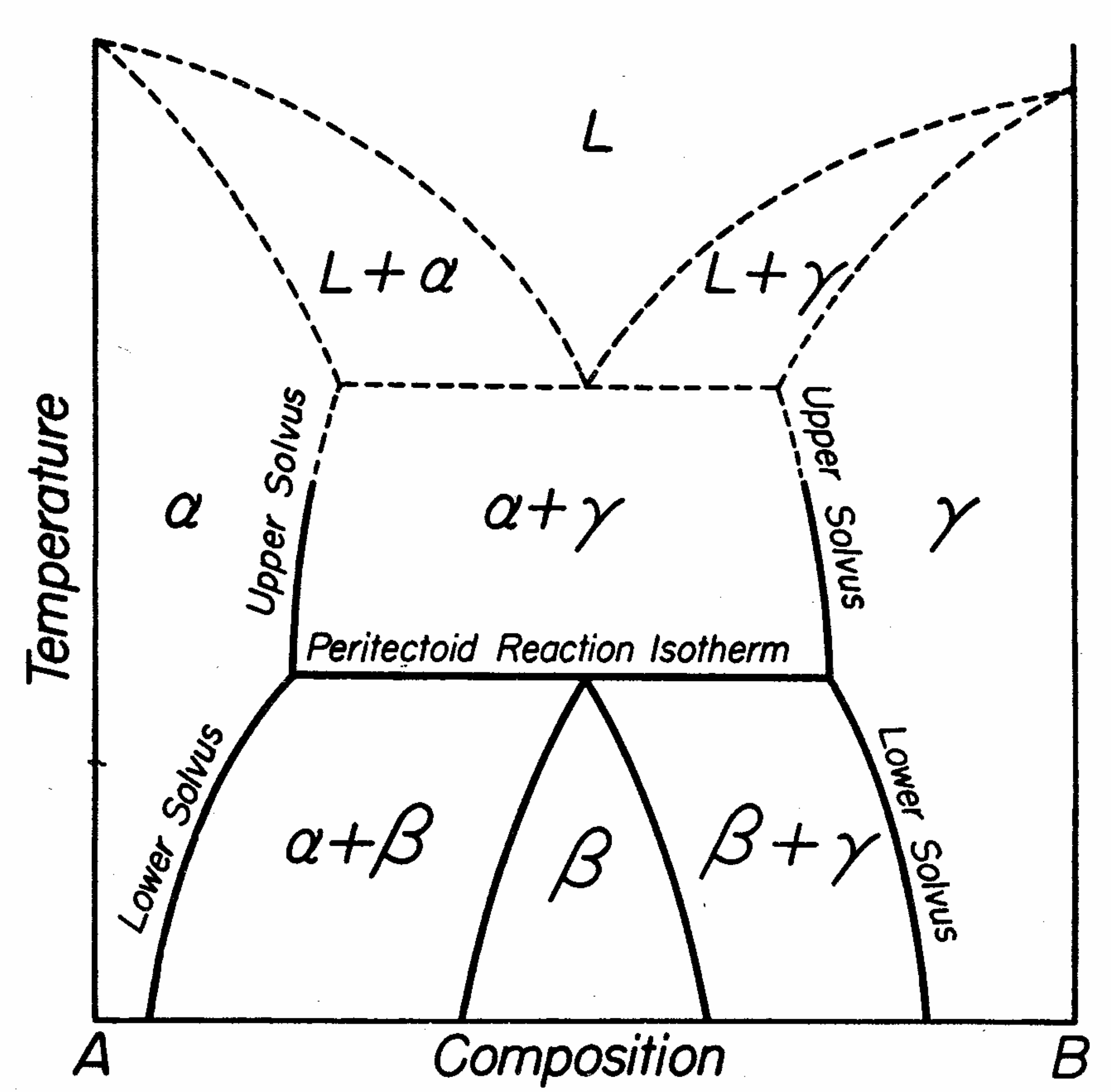
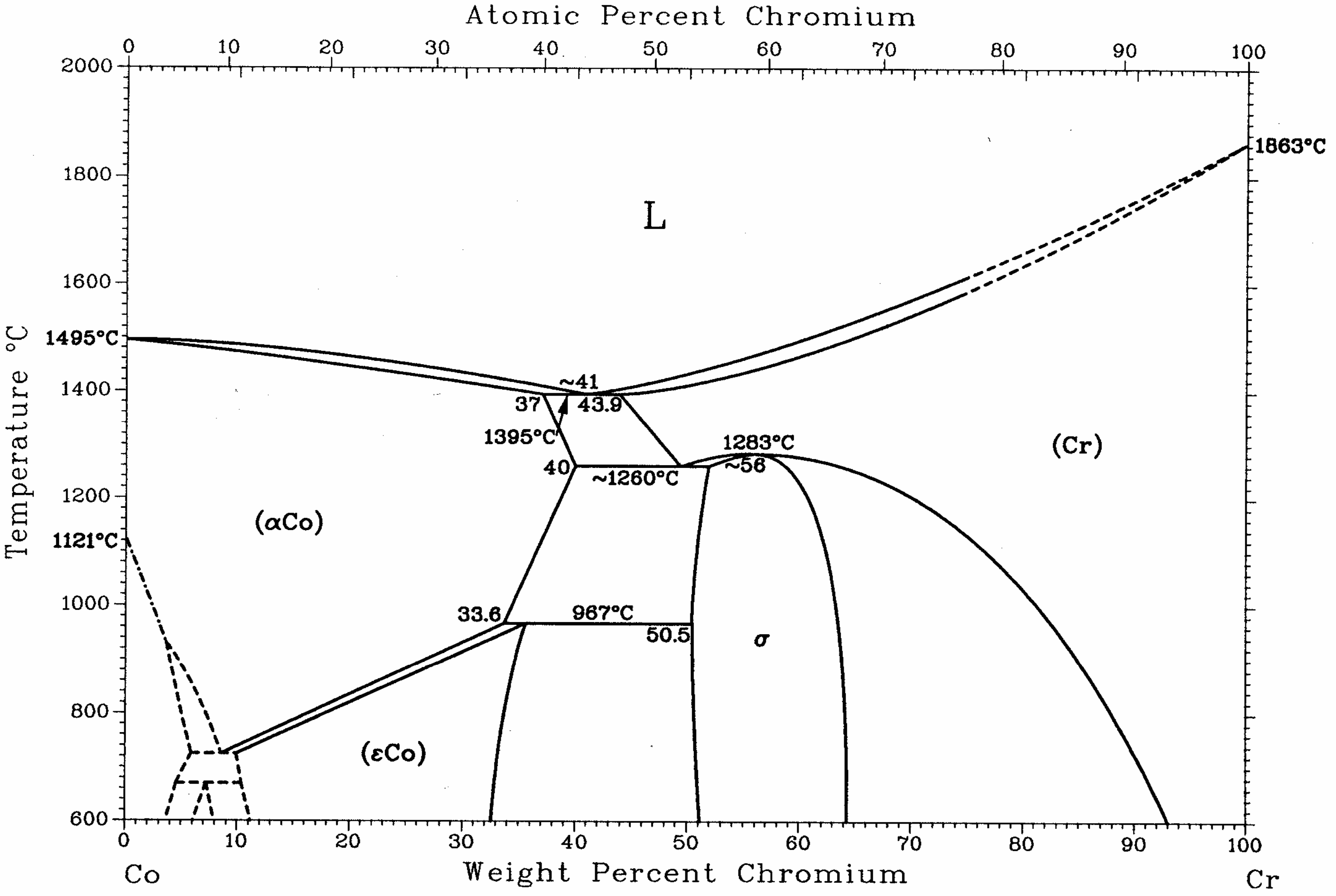


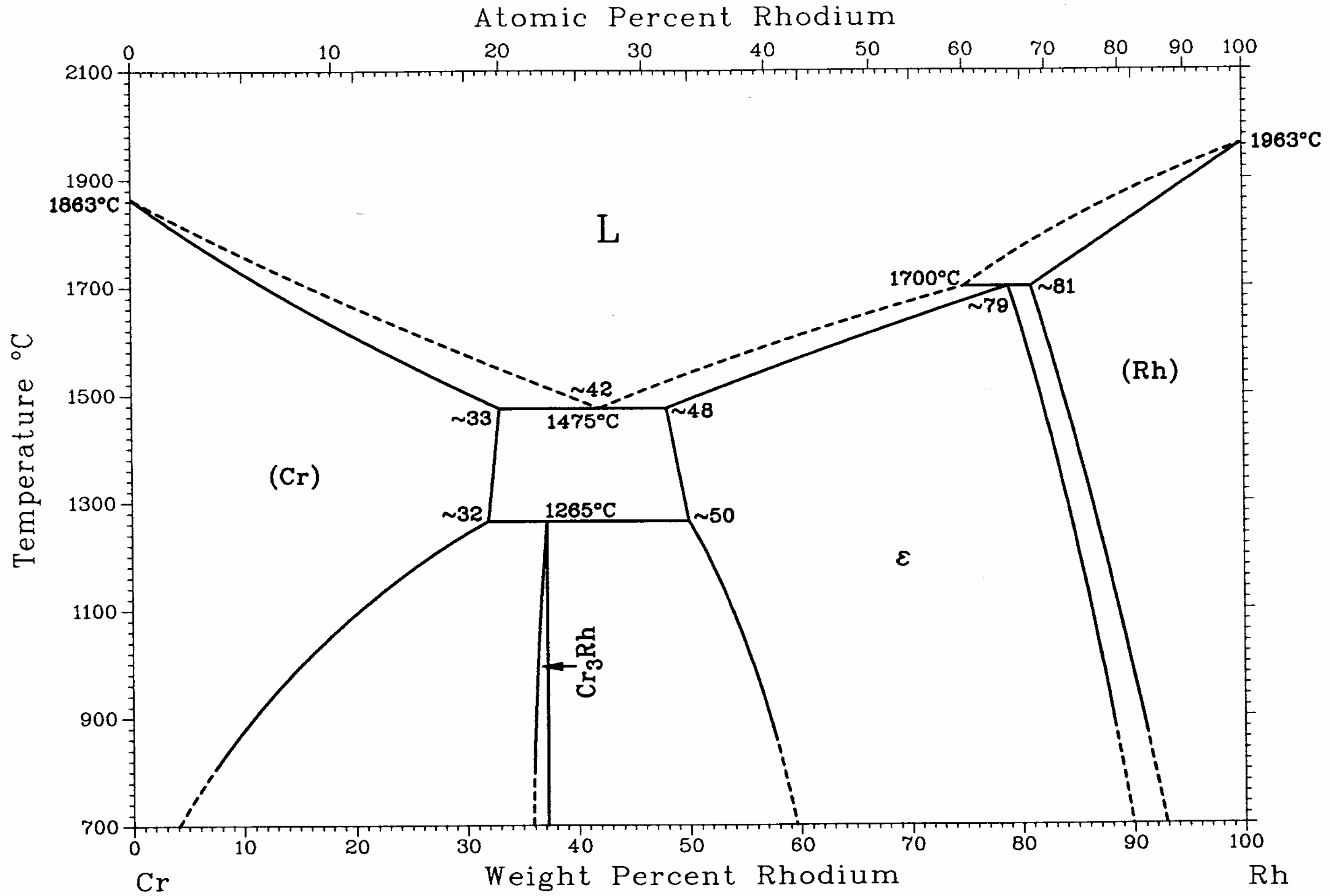
FIG. 9-1

$$\boxed{\alpha + \gamma \underset{\text{aquecimento}}{\overset{\text{resfriamento}}{\rightleftarrows}} \beta}$$

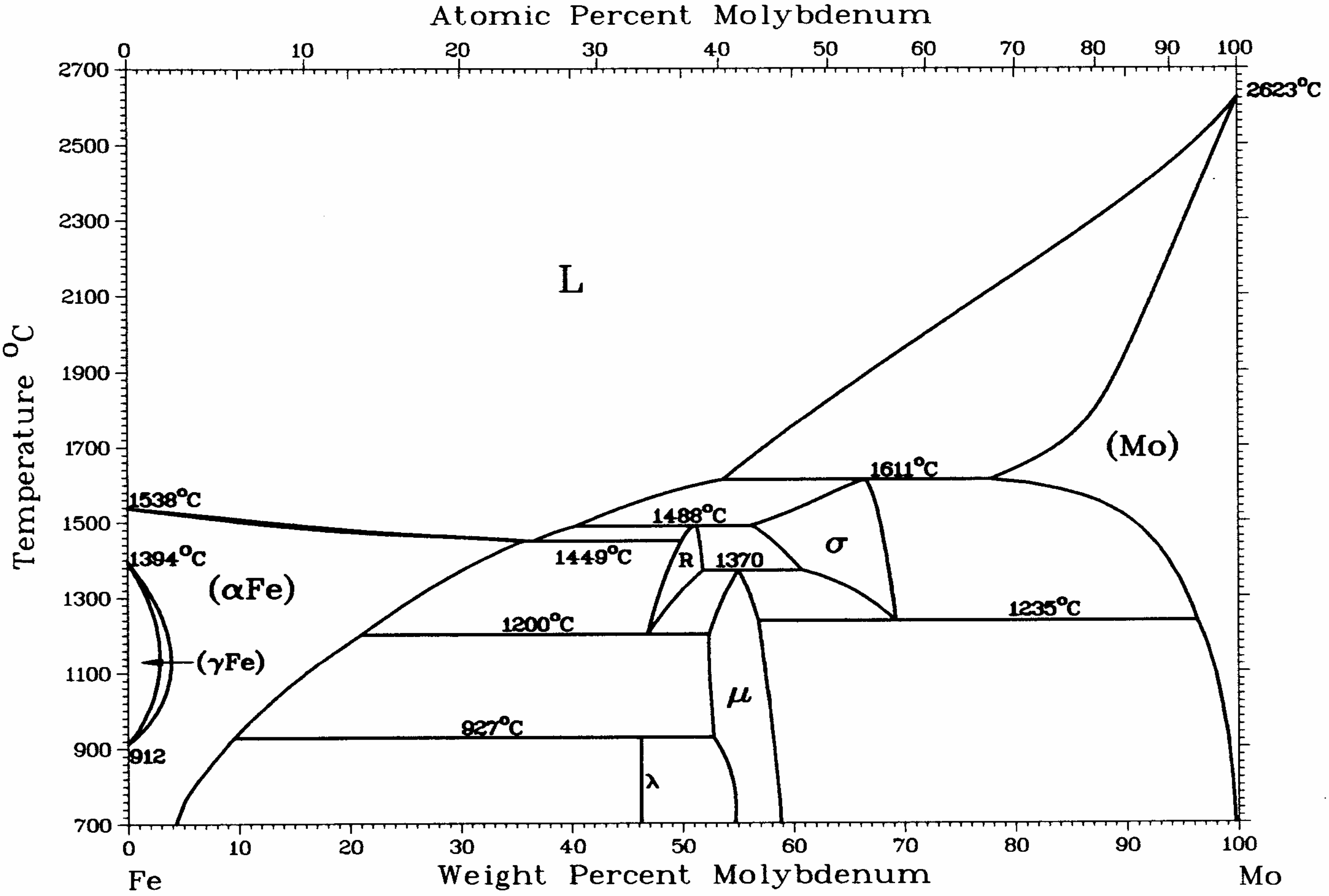
Co-Cr


Atomic Percent Chromium
0
10
20
30
40
50
60
70
80
90
100
2000
1800
1600
1495°C
1400
1200
1121°C
1000
800
600
Temperature °C
1863°C
L
~41
37
43.9
1395°C
40
~1260°C
1283°C
~56
(Cr)
(αCo)
33.6
967°C
50.5
σ
(εCo)
0
10
20
30
40
50
60
70
80
90
100
Co
Weight Percent Chromium
Cr

Cr-Rh

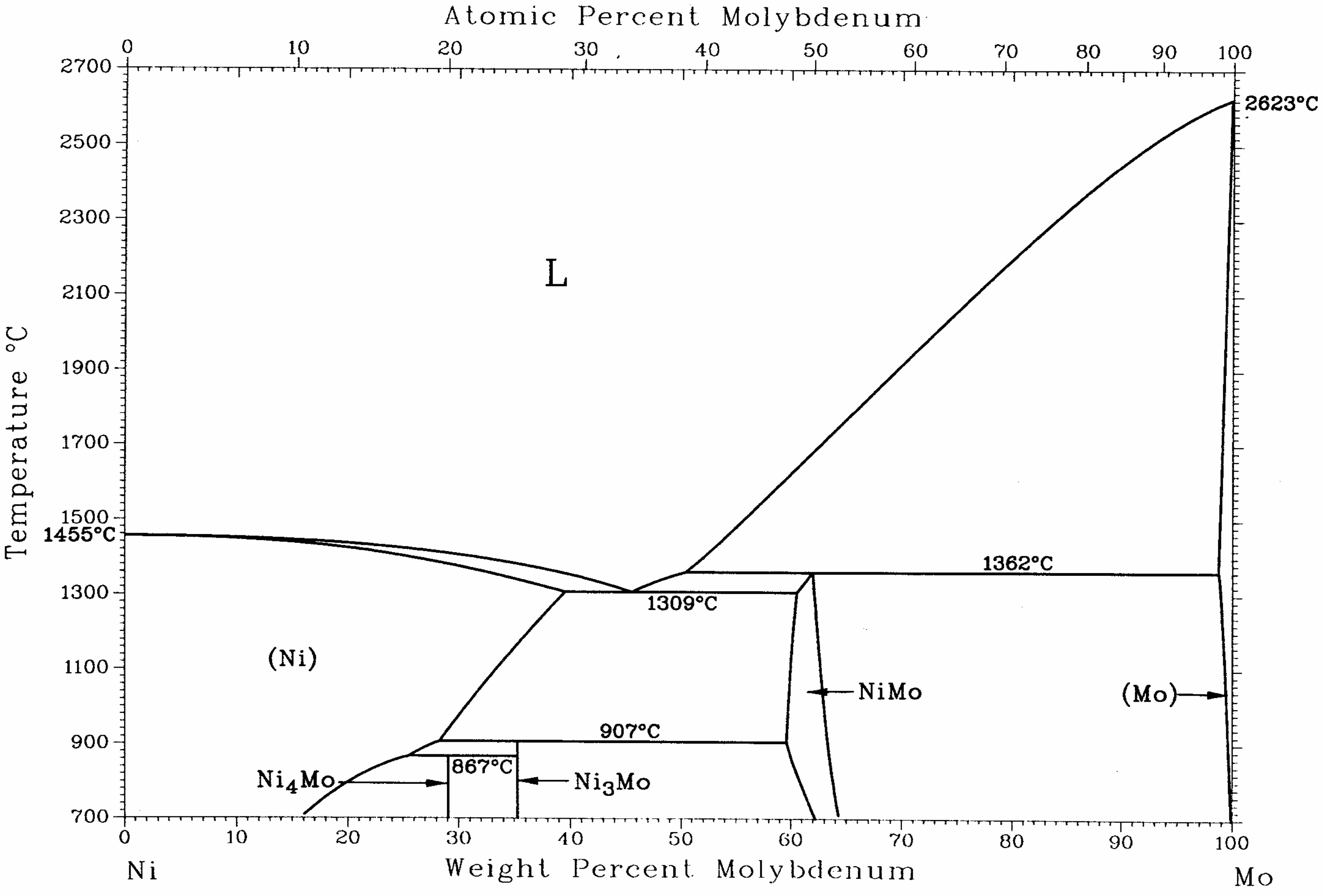

Atomic Percent Rhodium
0
10
20
30
40
50
60
70
80
90
100
2100
1900
1863°C
1700
1500
1300
1100
900
700
Temperature °C
1963°C
L
1700°C
~81
~79
(Rh)
~42
~33
1475°C
~48
(Cr)
~32
1265°C
~50
ε
Cr_3Rh
0
10
20
30
40
50
60
70
80
90
100
Cr
Weight Percent Rhodium
Rh

Fe-Mo



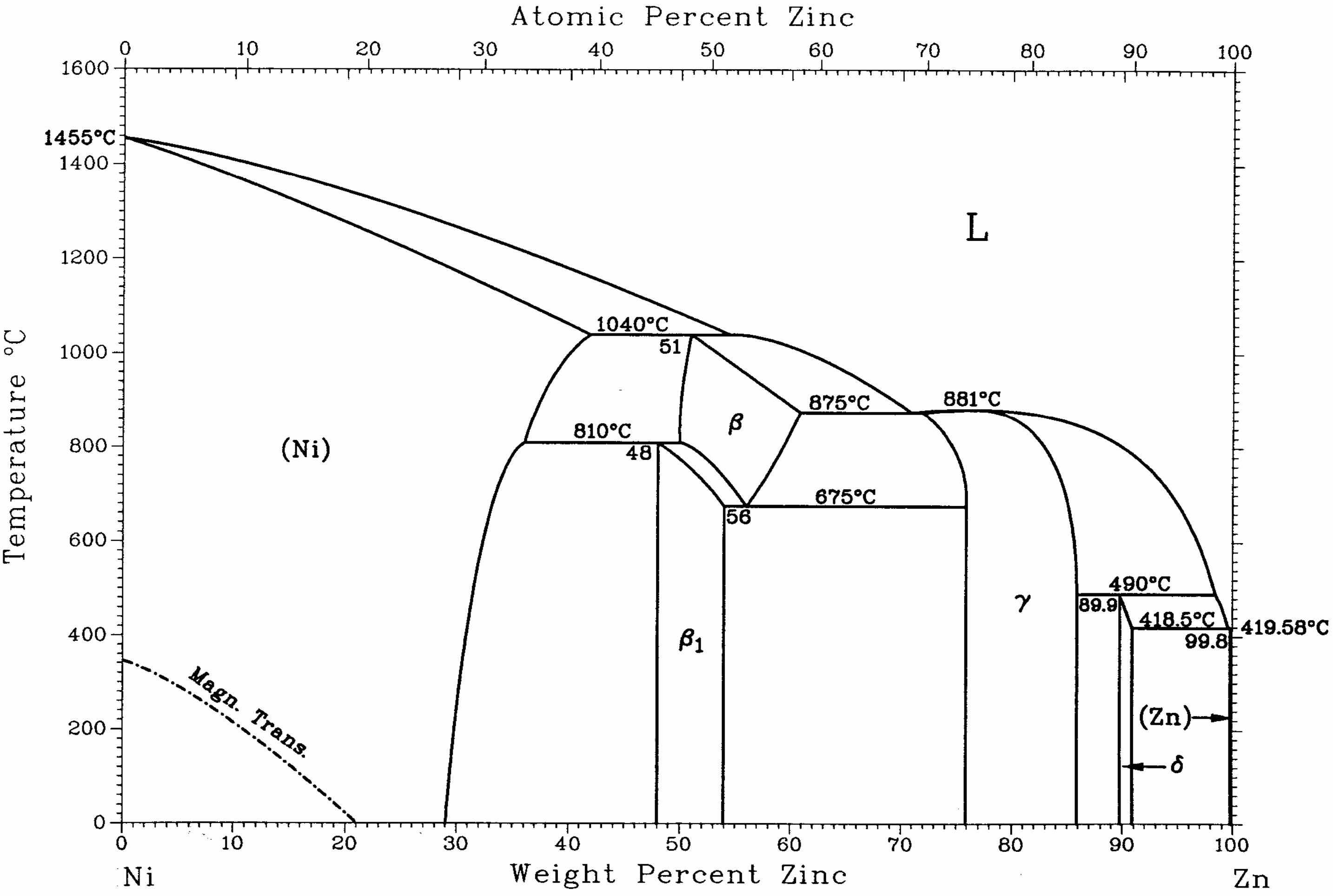
Atomic Percent Molybdenum
0
10
20
30
40
50
60
70
80
90
100
2700
2500
2300
2100
1900
1700
1500
1300
1100
900
700
Temperature °C
2623°C
L
(Mo)
1611°C
1538°C
1488°C
1500
1449°C
R
1370
σ
1394°C
(αFe)
1200°C
1235°C
(γFe)
μ
927°C
912
λ
0
10
20
30
40
50
60
70
80
90
100
Fe
Weight Percent Molybdenum
Mo

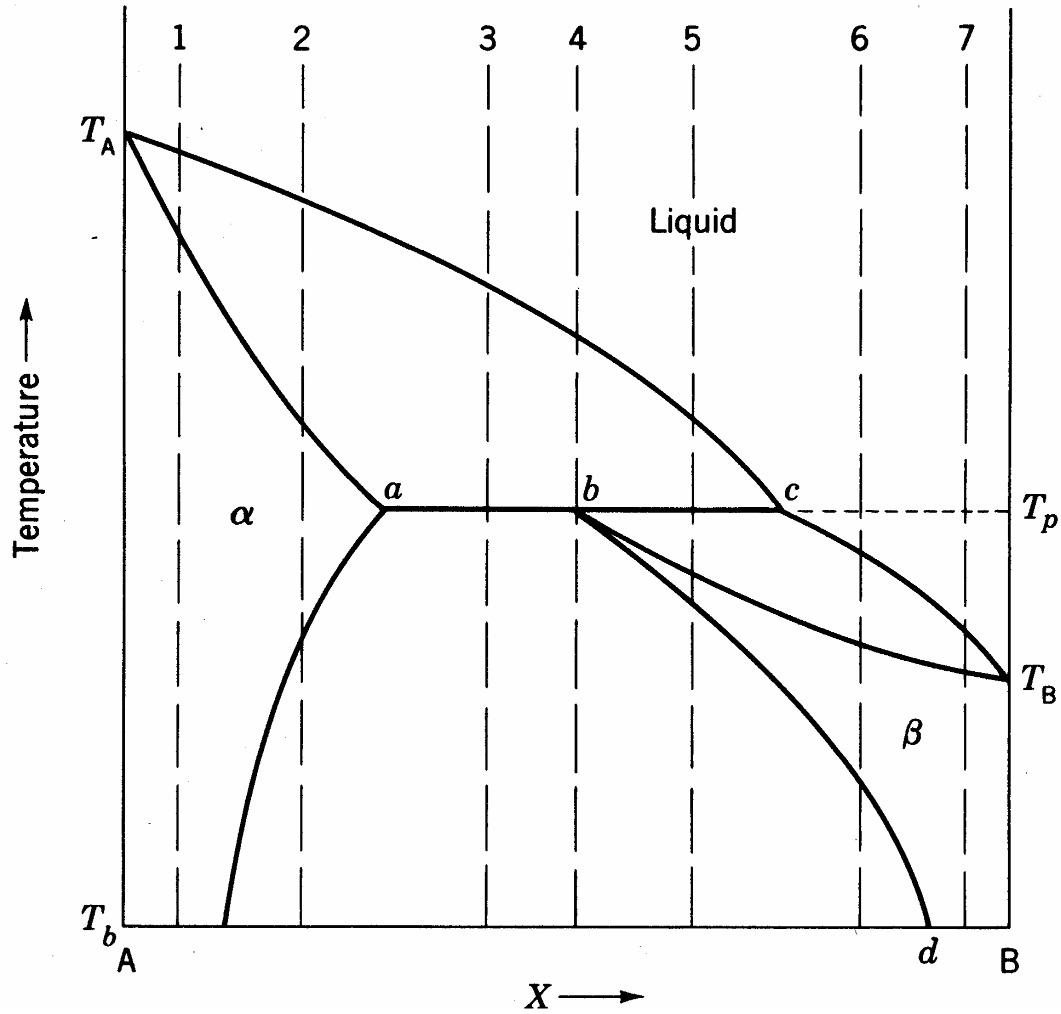
Mo-Ni



Atomic Percent Molybdenum
0
10
20
30
40
50
60
70
80
90
100
2700
2500
2300
2100
1900
1700
1500
1455°C
1300
1100
900
700
Temperature °C
2623°C
L
1362°C
1309°C
(Ni)
NiMo
(Mo)
907°C
867°C
Ni₄Mo
Ni₃Mo
0
10
20
30
40
50
60
70
80
90
100
Ni
Weight Percent Molybdenum
Mo

Ni-Zn


Atomic Percent Zinc
0
10
20
30
40
50
60
70
80
90
100
1600
1455°C
1400
1200
1000
800
600
400
200
0
Temperature °C
L
1040°C
51
810°C
48
β
875°C
881°C
675°C
56
(Ni)
β_1
γ
490°C
89.9
418.5°C
99.8
419.58°C
(Zn)
δ
Magn. Trans.
0
10
20
30
40
50
60
70
80
90
100
Ni
Weight Percent Zinc
Zn


1
2
3
4
5
6
7
T_A
Liquid
Temperature
a
b
c
T_p
α
T_B
β
T_b
A
d
B
X

10 - SISTEMAS SINTÉTICOS BINÁRIOS

$$L_I + L_{II} \underset{\text{aquecimento}}{\overset{\text{resfriamento}}{\rightleftarrows}} \beta$$

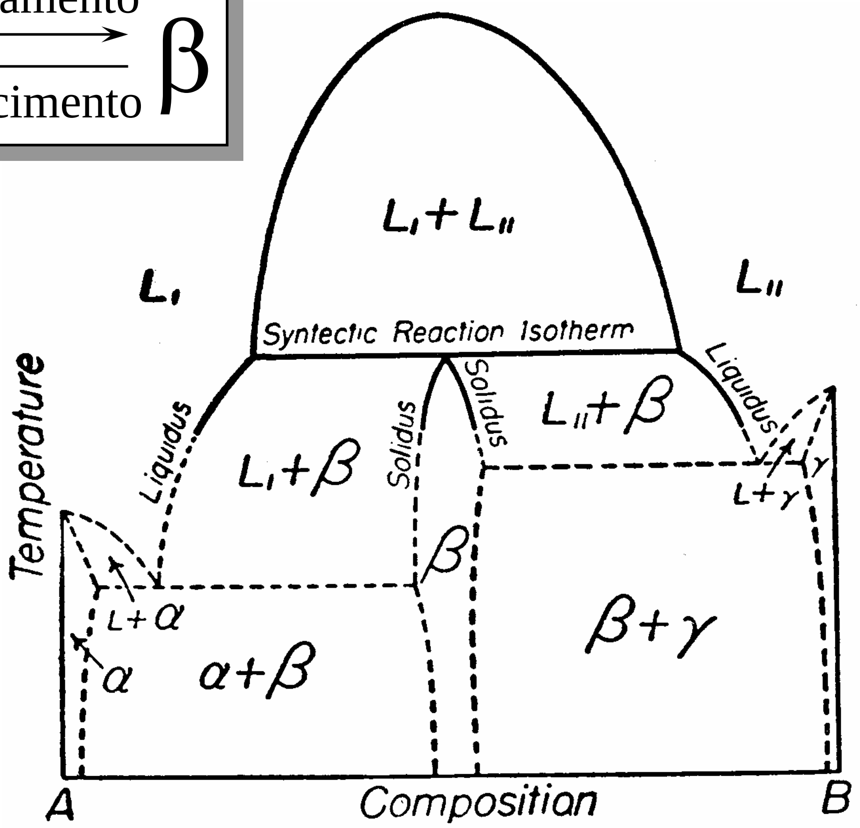
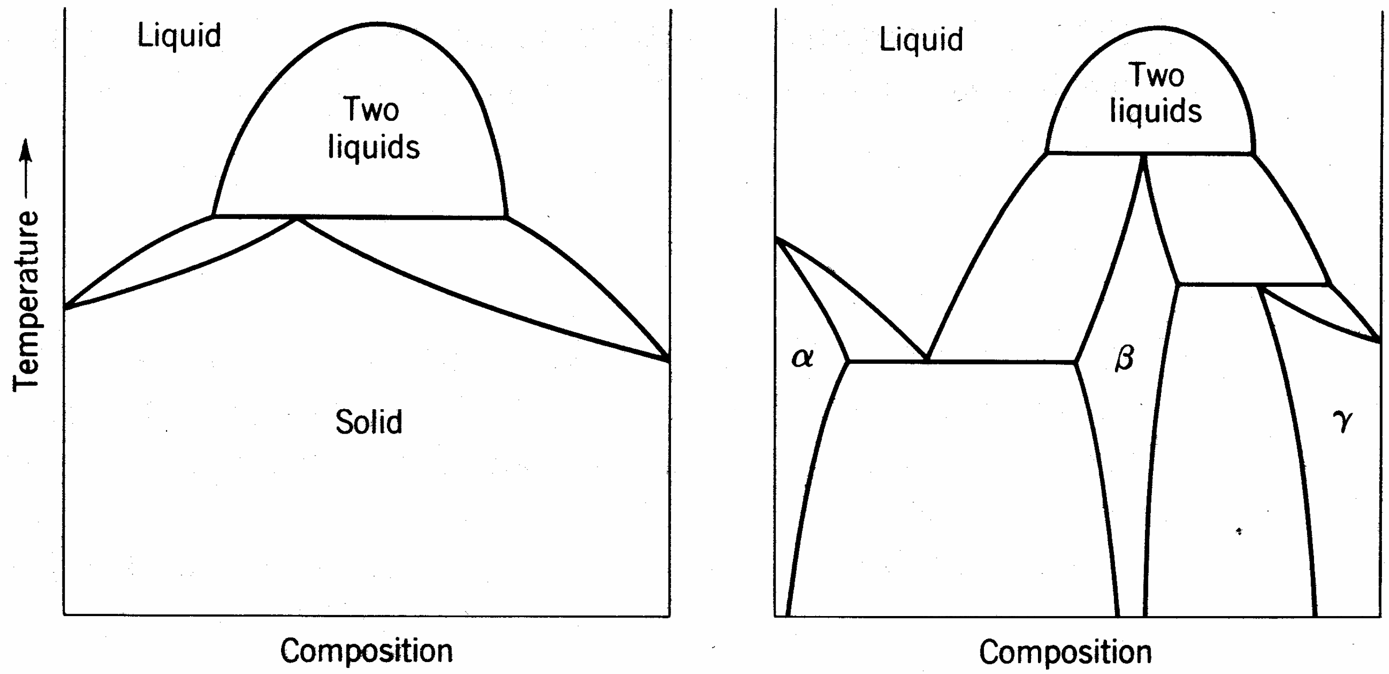
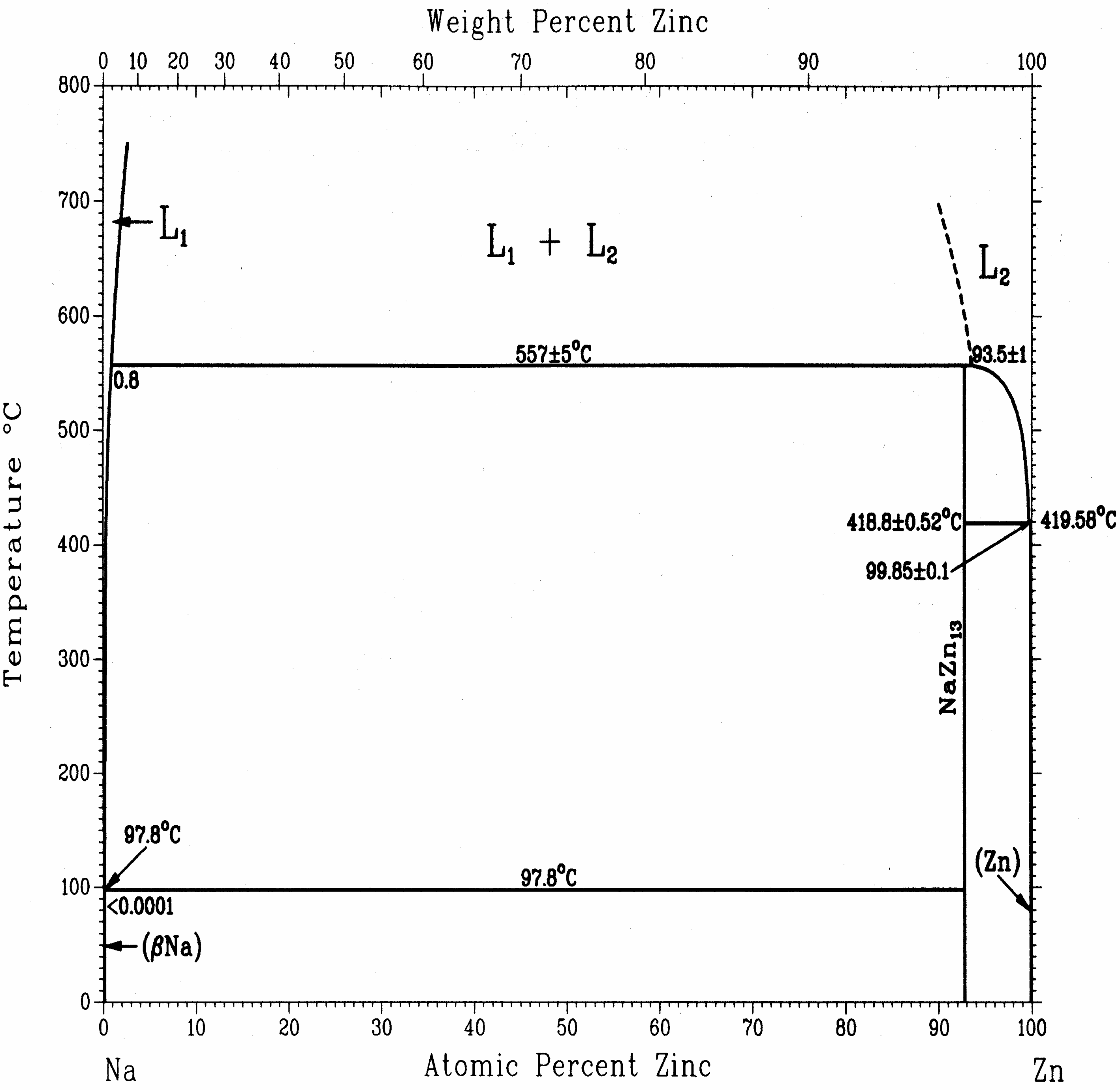


Fig. 10-1



(a) (b)

Fig. 7.8 *Two diagrams containing the syntectic invariant reaction.*


Weight Percent Zinc
0
10
20
30
40
50
60
70
80
90
100
Temperature °C
800
700
600
500
400
300
200
100
0
L₁
L₁ + L₂
L₂
557±5°C
0.8
93.5±1
418.8±0.52°C
419.58°C
99.85±0.1
NaZn₁₃
97.8°C
97.8°C
<0.0001
(βNa)
(Zn)
Atomic Percent Zinc
0
10
20
30
40
50
60
70
80
90
100
Na
Zn