

Chalmers University of Technology
Department of Materials and Manufacturing Technology

Examination in Phase Transformations MMK162
Advanced Engineering Materials
13.00-17.00, 31 October 2014

Aid permitted at examination: Electronic calculator of the simple type approved by Chalmers

Solutions and answers should be well worked out and motivated to get full credit.

The question pages must be submitted together with the written answers.

In the headlines below preliminary credits are given, this might be changed during correction. Solutions will be displayed on course homepage.

Assignments	Credit
1. Phase diagrams and free energy curves	10
2. Diffusion	10
3. Interfaces and microstructure	6
4. Solidification	8
5. Diffusional transformations	8
6. Diffusionless transformation	3
7. Novel metallic materials	2
8. Solid/gas interactions	3
Sum:	50

Limits for: 3>45%
 4>60%
 5>80%

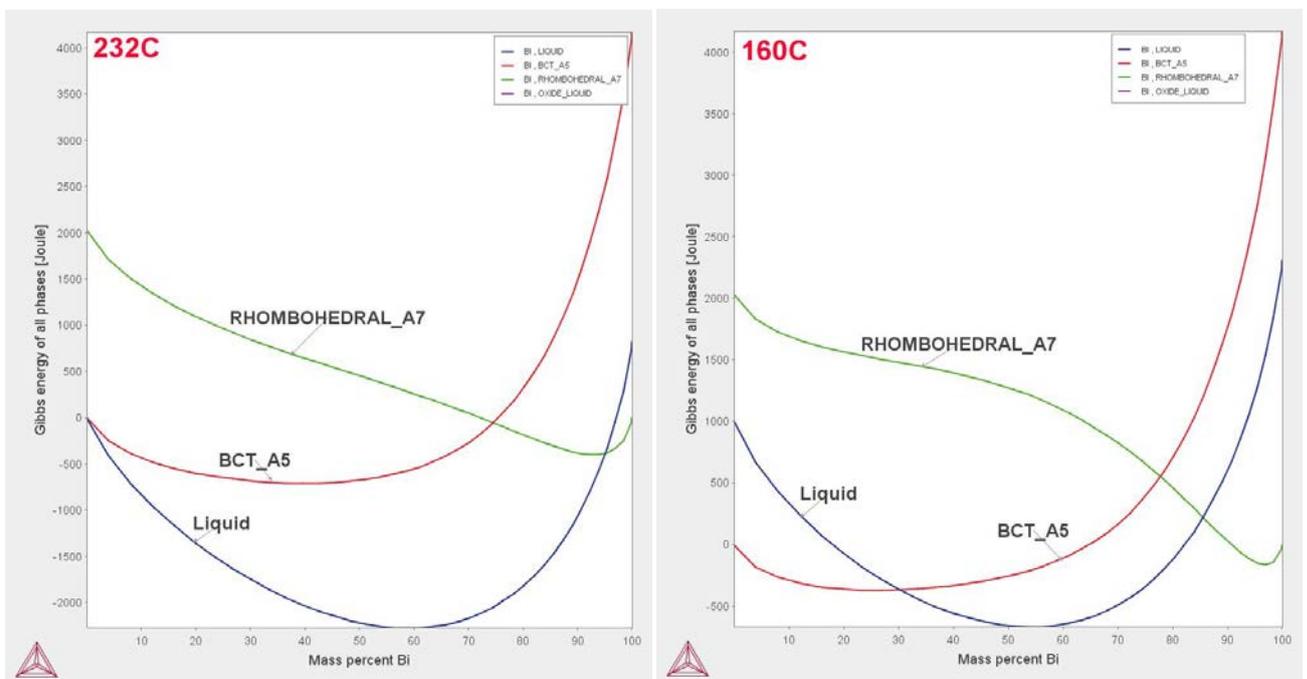
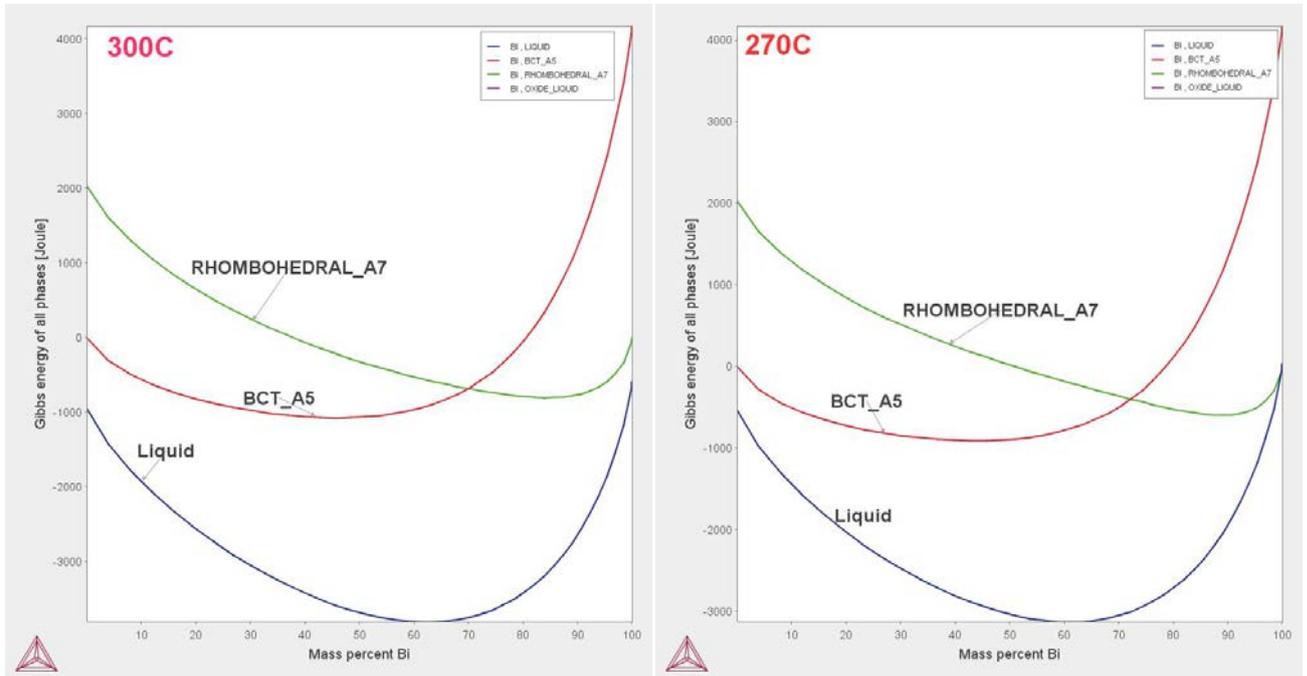
Grading will be based on the total sum of **50 points**. Bonus points earned during lectures (quiz) will be added to the exam points.

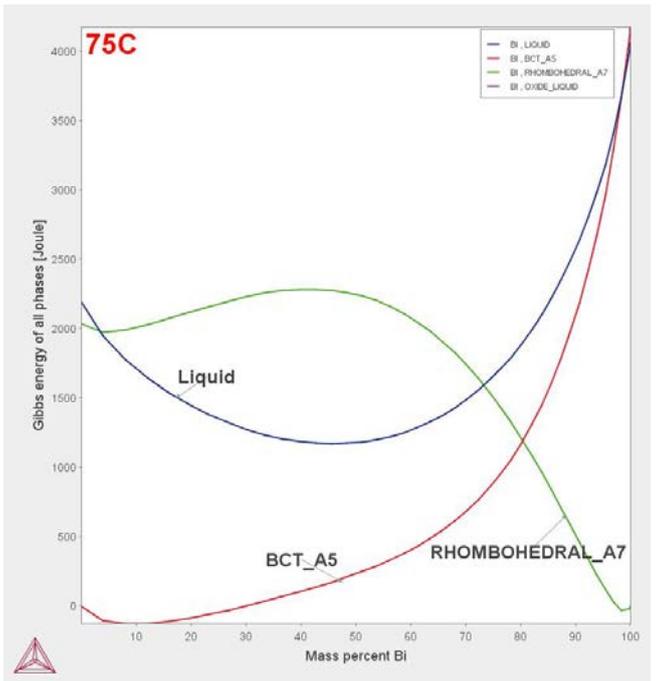
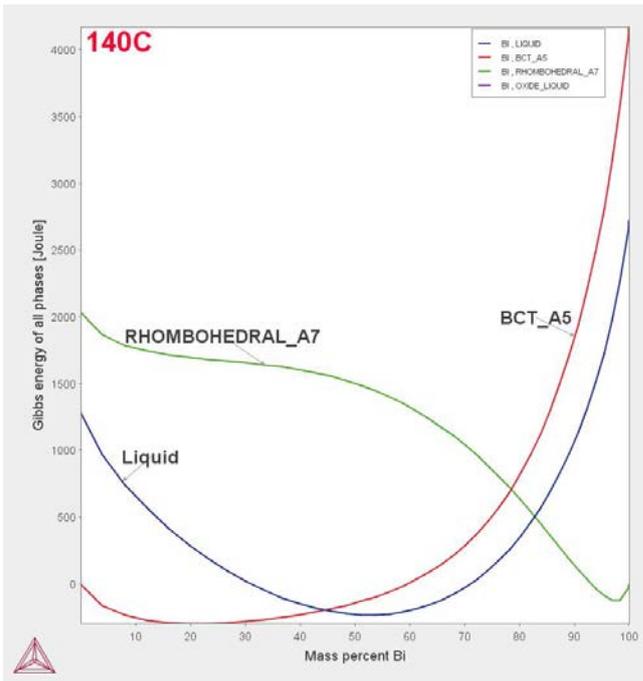
Göteborg, 2014.10.23

Eduard Hryha

1. Phase diagrams and free energy curves (10 p)

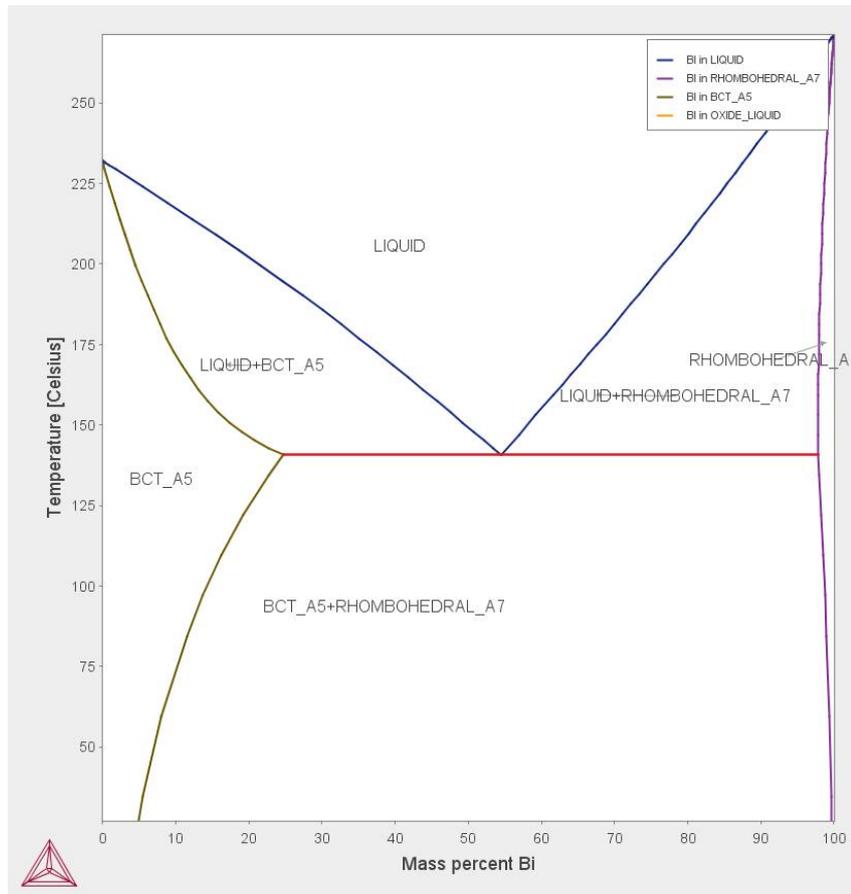
- Derive phase diagram for Sn-Bi system using free energy diagrams according to the figure below. Respective temperatures are 300, 270, 232, 160, 140 and 75°C (marked on the top of each figure). X and Y-axes should be drawn in correct scale compared to the phase diagram. (5)
- Mark chemical potentials of the phase equilibria for the free energy diagrams at 160°C. (1 p)



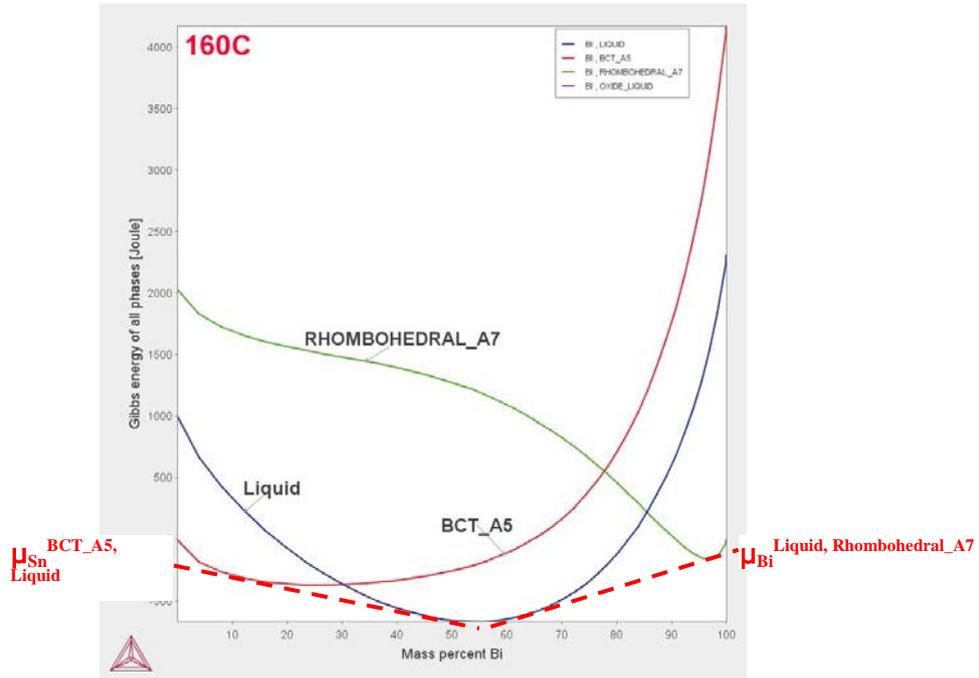


Answers:

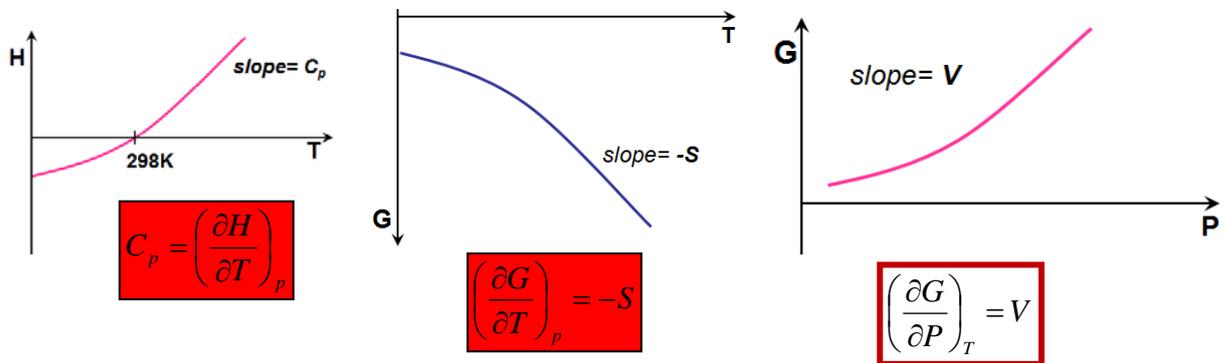
a)



b)



c) Plot schematically dependence of $H=f(T)$, $G=f(T)$ and $G=f(P)$ and indicate how slope of these thermodynamic properties is expressed. (2p)



d) Estimate the change in equilibrium melting temperature of nickel for change in pressure $\Delta P=1000 \text{ bar}$, $L=17.48 \text{ kJ}\cdot\text{mol}^{-1}$, $T_m=1455 \text{ }^\circ\text{C}$, $V_L=7.43 \text{ cm}^3$ and $V_s=6.59 \text{ cm}^3$. (2p)

Answer: Clausius-Clapeyron equation

$$\left(\frac{\partial P}{\partial T} \right)_{eq} = \frac{\Delta H}{T \Delta V} \rightarrow \frac{\Delta P}{\Delta T} = \frac{L}{T \Delta V} \rightarrow$$

$$\Delta T = \frac{\Delta P T \Delta V}{L} = \frac{10^8 (\text{Pa}) * 1728 (\text{K}) * 0.84 * 10^{-6} (\text{m}^3)}{17480 \left(\frac{\text{J}}{\text{mol}} \right)} = 8,3 \text{ K}$$

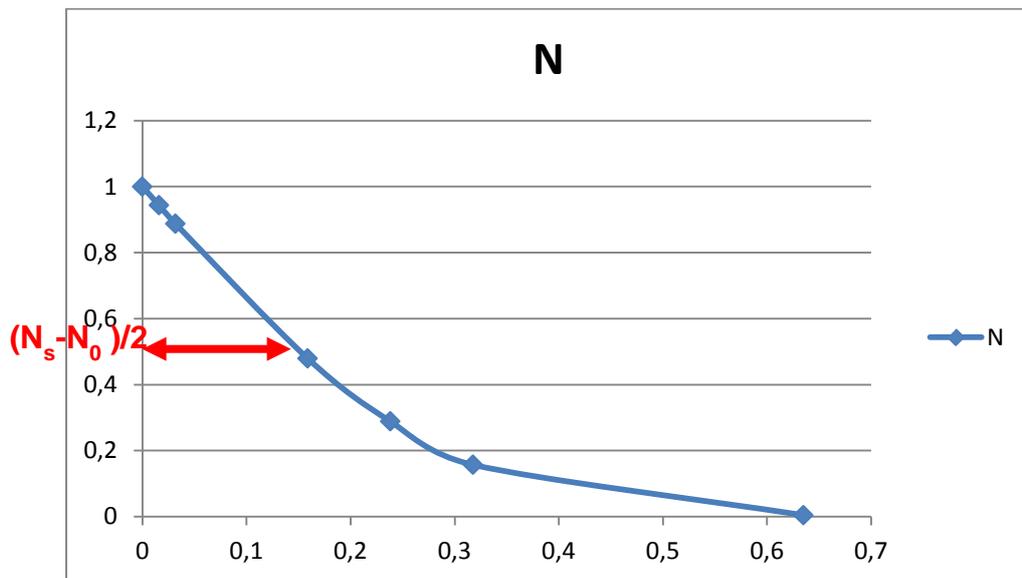
2. Diffusion (10 p)

- a) Calculate and sketch concentration profile of nitrogen after nitriding of the steel in the ammonia-containing atmosphere at 900°C for 1 hour. Nitrogen potential of the atmosphere is constant and equal to 1%. Steel is nitrogen-free. Diffusion coefficient of nitrogen in austenite at this temperature is $D=7 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$. (5 p)

$$N = N_s - (N_s - N_0) \operatorname{erf} \frac{x}{2\sqrt{Dt}}$$

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2) dy$$

N_0	N_s	z	erf	D	t	Dt	2sqrt(Dt)	N, %	x (mm)
0	1	0	0	7,00E-12	3600	2,52E-08	0,000317	1	0
0	1	0,05	0,0564	7,00E-12	3600	2,52E-08	0,000317	0,9436	0,015875
0	1	0,1	0,1125	7,00E-12	3600	2,52E-08	0,000317	0,8875	0,031749
0	1	0,5	0,5205	7,00E-12	3600	2,52E-08	0,000317	0,4795	0,158745
0	1	0,75	0,7112	7,00E-12	3600	2,52E-08	0,000317	0,2888	0,238118
0	1	1	0,8427	7,00E-12	3600	2,52E-08	0,000317	0,1573	0,31749
0	1	2	0,9953	7,00E-12	3600	2,52E-08	0,000317	0,0047	0,63498



- b) Define on the sketch the thickness of the nitrided layer and calculate it for presented case. (1 p)

See sketch above, $(N_s - N_0)/2 \rightarrow x \approx \sqrt{Dt} = 1,59E-04 \text{ (m)}$

- c) Describe diffusion in substitutional alloys, sketch fluxes of the atoms of two inter-diffusing phases and their relation to the flux of vacancies. Motivation and presentation of respective equations is required to obtain full credit. (4 p)



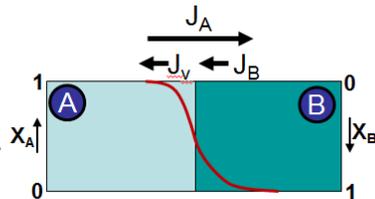
Diffusion in substitutional alloys

- atoms B diffuses in solvent A;
- rate of B into vacant site \neq rate of A into vacant site \rightarrow intrinsic diffusivities $D_A \neq D_B$;
- D_A and D_B are defined in a way that Fick's 1-st law applies to diffusion **relative to the lattice**;
- fluxes across a given plane:

$$J_A = -D_A \frac{\partial C_A}{\partial x}$$

$$J_B = -D_B \frac{\partial C_B}{\partial x}$$

Interdiffusion of A and B in a diffusion couple \rightarrow welding together blocks of pure A and B



Assume that total number of atoms is constant and independent of composition:

$$C_0 = C_A + C_B$$

$$\frac{\partial C_A}{\partial x} = -\frac{\partial C_B}{\partial x}$$

Concentration gradients driving diffusion are equal but opposite \rightarrow fluxes **relative to the lattice**:

$$J_A = -D_A \frac{\partial C_A}{\partial x}$$

$$J_B = D_B \frac{\partial C_A}{\partial x}$$



Diffusion in substitutional alloys

- consider case $D_A > D_B \rightarrow |J_A| > |J_B|$;
- when atom moves = vacancy moves \rightarrow atom flux in one direction is equal to vacancies flux in opposite direction:

$$J_v = -J_A - J_B = (D_A - D_B) \frac{\partial C_A}{\partial x}$$

variation of vacancies flow across diffusion couple;

Vacancy movement = lattice movement

rate of vacancies creation/destruction:

$$\frac{\partial C_v}{\partial t} = -\frac{\partial J_v}{\partial x}$$

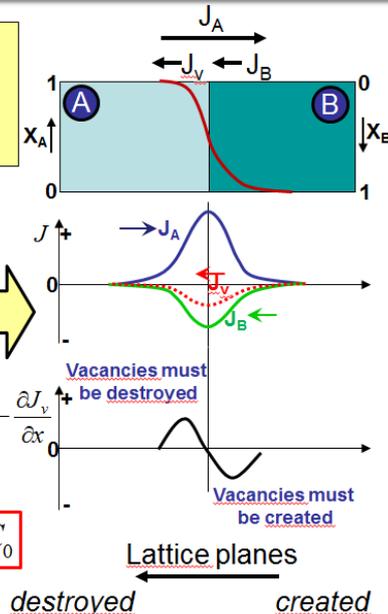
speed of lattice v = flux of vacancies crossing it:

$$J_v A \delta t = A v \delta t C_0 \rightarrow J_v = v C_0$$

[Darken 1-st eq]

$$X_A = \frac{C_A}{C_0}$$

$$v = (D_A - D_B) \frac{\partial X_A}{\partial x}$$



Darken 1-st eq
$$v = (D_A - D_B) \frac{\partial X_A}{\partial x}$$

Darken 2-nd eq.
$$\tilde{D} = X_B D_A + X_A D_B$$

3. Interfaces and microstructure (6p)

- a) Sketch two-dimensional grain boundary configuration for the grain having 3, 4, 6 and 8 neighboring grains and indicate directions of grain boundary migration. Explain which grains will grow and why. (2p)

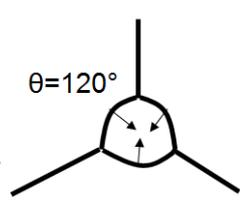

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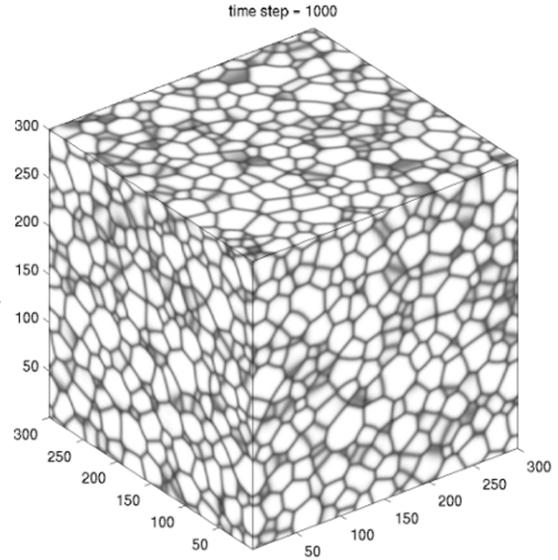
Thermally Activated Migration of Grain Boundaries

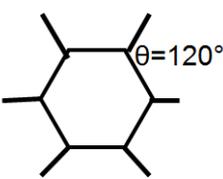
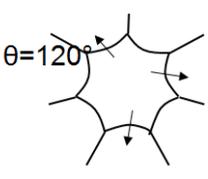
$$\frac{\gamma_{23}}{\sin \theta_1} = \frac{\gamma_{13}}{\sin \theta_2} = \frac{\gamma_{12}}{\sin \theta_3} \Rightarrow \theta = 120^\circ$$

Surface tension must also balance: ΔP caused by curved boundary:

Migration towards curvature





Larger grains >6 neighbours = growth!!!

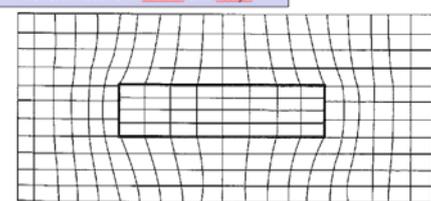
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Crystal Interfaces and Microstructure
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- b) Describe the effect of coherency loss during precipitate growth based on the change in the Gibbs free energy change of the system. Sketch and define critical radius for the precipitate to lose its coherency. Motivation and presentation of respective equations is required to obtain full credit. (4p)


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Coherency Loss

Fig 3.51. From: D.A. Porter, etc. Phase transformations in metals and alloys



Large coherency strains parallel to the plate due to misfit across broad faces → increase with plate thickness → high shear stresses at the corners of the plate → energetically favourable for broad faces to become semicoherent

Aluminum-copper precipitation sequence. fcc, face-centered cubic; bct, body-centered tetragonal

Ref: ASM Handbook, Vol.3, Precipitation Hardening of Aluminum Alloys

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Coherency Loss

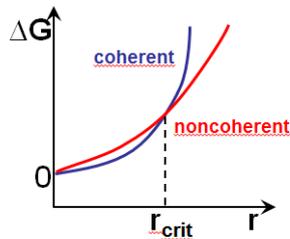
Coherent interfaces → low interfacial energy but presence of coherency strain energy

Incoherent interfaces → higher surface energy but coherency strain energy is absent

Critical size for coherency loss?

Balance between γ (coherent) and γ (incoherent)

For a particle of radius r :



$$\Delta G(\text{coherent}) = 4\pi r^2 \cdot \gamma_{ch} + 4\mu\delta^2 \cdot \frac{4}{3}\pi r^3$$

$$\Delta G(\text{incoherent}) = 4\pi r^2 (\gamma_{ch} + \gamma_{st}) + 0$$

$$r_{crit} = \frac{3\gamma_{st}}{4\mu\delta^2}$$

At the critical radius

$$\Delta G(\text{coherent}) = \Delta G(\text{incoherent})$$

For small δ → semicoherent interface will be formed first with the structural energy

$$\gamma_{st} \propto \delta$$

Critical radius for semicoherent interface

$$r_{crit} \propto \frac{1}{\delta}$$

4. Solidification (8 p)

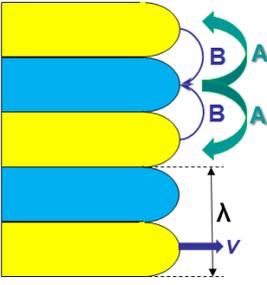
a) Describe eutectic solidification:

- i. conditions for formation of the normal or anomalous eutectic, conditions for the formation of lamellar or fibrous structure. (1p)
 - **normal** eutectic → two phases appear as alternate lamellae or rods of minor phase embedded in matrix → both phases have low entropies of fusion;
 - **anomalous** eutectic → one phase is faceted → has high entropy of fusion → flaked (irregular lamellar) structures
 - if volume fraction of one phase is significantly lower than that of the other < 0.28 → fibrous structure

- ii. sketch the effect of the interlamellar spacing on the Gibbs free energy of the system during eutectic solidification and present relevant equations. Motivation is required to get full credit. (3p)

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Eutectic Solidification



- smaller interlamellar spacing → faster diffusion → fastest growth;
- limit of λ → interfacial energy $\gamma_{\alpha\beta} \rightarrow 2/\lambda$ [m²] → total amount of α/β interface per m³ of eutectic;
- free energy change associated with solidification of 1 mol eutectic:

$$\Delta G(\lambda) = -\Delta G(\infty) + \frac{2\gamma_{\alpha\beta}V_m}{\lambda}$$

- $\Delta G(\infty)$ - free energy decrease for $\lambda \rightarrow \infty$ - driving force - must compensate interfacial energy;

If total undercooling is $\Delta T_{0|v}$ $\Delta G(\infty) = \frac{\Delta H \cdot \Delta T_0}{T_E}$

The minimum possible spacing λ^* is obtained when $\Delta G(\lambda^*) = 0$:

$$\lambda^* = \frac{2\gamma_{\alpha\beta}V_mT_E}{\Delta H \cdot \Delta T_0}$$

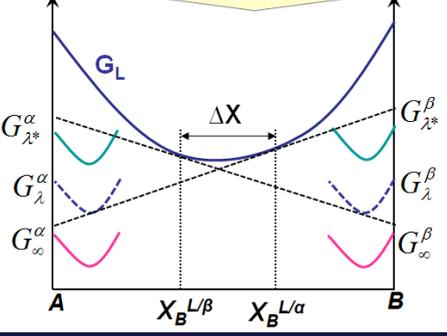
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Eutectic Solidification

- if $\lambda = \lambda^* \rightarrow$ infinitely slow growth \rightarrow liquid in contact with both phases has the same composition X_E ;
- if $\lambda > \lambda^* \rightarrow$ lower free energy locked in interface $\rightarrow G^\alpha$ and G^β are reduced \rightarrow difference in liquid composition in equilibrium with growing phases \rightarrow liquid in local equilibrium with α has composition $X_B^{L/\alpha} \rightarrow$ rich in solute B:

diffusion control \rightarrow rate is determined by liquid diffusivity and concentration gradient ($\Delta X = X_B^{L/\alpha} - X_B^{L/\beta}$)

$$v = k_1 D \frac{\Delta X}{\lambda}$$



- varying interface undercooling $\Delta T_0 \rightarrow$ growth rate v and spacing λ can be varied independently \rightarrow it is impossible to predict the spacing that will be observed for a given growth rate

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b) When a material is welded, the microstructure formed in the weld may look like the image in Fig.1

i. What are the factors influencing the weld microstructure? Motivate your answer. (2 p)

- rate of heat input (process, size etc);
- v : speed of arc movement;
- K_s : thermal conductivity of welded metal
- t : thickness of welded plate material type;
- grains tend to grow in direction normal to the solid/liquid interface;
 - preferred crystallographic growth direction - $\langle 100 \rangle$ for cubic – columnar growth;
 - no nucleation barrier;
 - determined by the grain size of the base metal.

ii. Indicate in which case the welding speed was higher? Lower? Is any effect of material type? If yes, describe its effect on isotherms. Motivate your answer. (2 p)

(a)– slowest, (c) – fastest

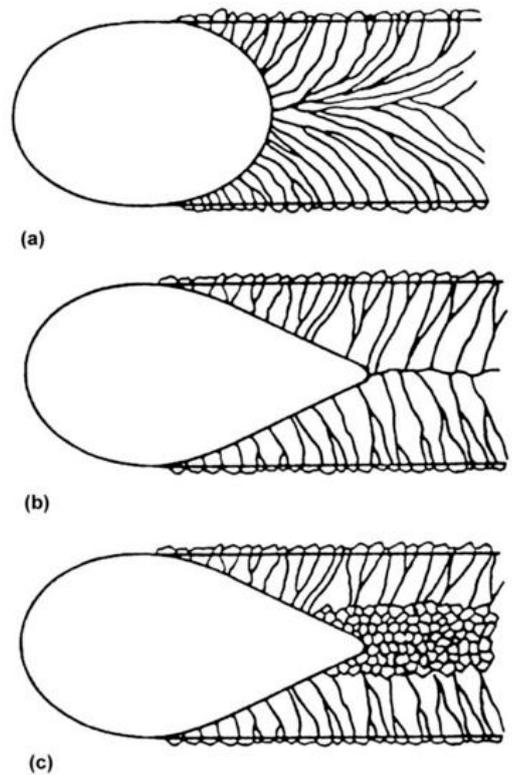


Fig. 1. Types of grain morphologies that can form in fusion welds [ASM Handbook, Vol.6a – Matsuda]

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Heat Flow in Welding

Thermal conductivity (material type) effect:

- temperature spreads over a larger area and causes a larger weld pool (larger weld bead) for low-conductivity material;
- isotherm contours elongate more toward the back of the arc for low-conductivity material;
- for aluminum, a larger heat input would be required to obtain the same weld size as the stainless steel weldment.

1 mm/s	5 mm/s	8 mm/s
<p>304 stainless steel</p>	<p>304 stainless steel</p>	<p>304 stainless steel</p>
<p>Steel</p>	<p>Steel</p>	<p>Steel</p>
<p>Aluminum</p>	<p>Aluminum</p>	<p>Aluminum</p>

ASM Handbook - Volume 6A, Welding Fundamentals and Processes -> Heat Flow in Fusion Welding -> Parametric Effects

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5. Diffusional transformations (8 p).

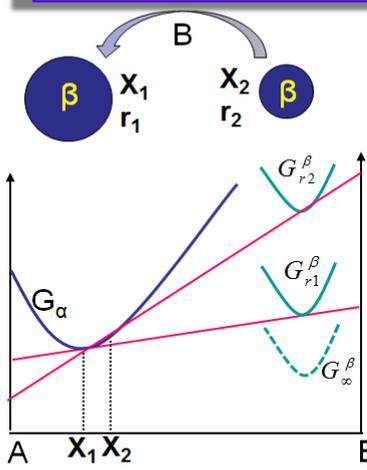
- a) Describe Gibbs-Thomson effect and sketch Gibbs energy curves for precipitates of different shape/size. Based on it define Ostwald ripening. (4 p)



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Particle Coarsening



High-density of fine precipitates tend to coarsen → decrease interfacial area → Ostwald ripening; Gibbs-Thomson effect: solute concentration in the matrix increases with particle size decreasing: $X_1 < X_2$; concentration gradient → solute diffuse to larger precipitates → coarsening of large precipitates; result: total number of particles decrease as the mean radius increases with time:

Assuming volume diffusion is rate controlling, it was shown:

$\bar{r}^3 - r_0^3 = kt$

$k \propto D\gamma X_e$

- $r=r_0$ at $t=0$;

- X_e – equilibrium solubility of very large particle.

D and X_e increase exponentially with T , coarsening rate:

$\frac{d\bar{r}}{dt} \propto \frac{k}{\bar{r}^2}$

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Diffusional Transformations in Solids

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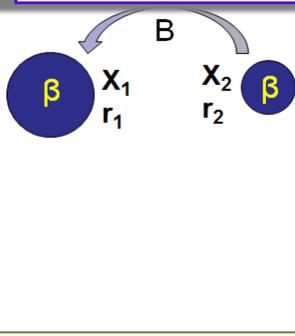
- b) Give an example how fine precipitates can be stabilized in steel matrix. Motivate your answer. (2p)



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Particle Coarsening



$\frac{d\bar{r}}{dt} \propto \frac{k}{\bar{r}^2}$

$k \propto D\gamma X_e$

Stabilization of fine precipitates:

Low γ : interfacial energy;

D : diffusion coefficient;

X_e : equilibrium solubility of $r=\infty$

- fully coherent precipitates;

- minimal misfit;

- **Nimonic** alloys: $Ni_3(TiAl)$ (γ') – fully coherent with fcc Ni-matrix - good creep resist.

- strong carbide-formers – stabilize cementite due to much lower diffusion of substitutional elements;

- low-alloyed steels.

- oxides are very insoluble in metals – low X_e ;

- fine oxide dispersions in the matrix – high strength at high T ;

- W and Ni strengthened by ThO_2 .

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Diffusional Transformations in Solids

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- c) Describe differences in the nucleation and growth of the pearlite and bainite based on the orientational relationship to the parent grain. Describe the main differences in the structure between the pearlite and bainite, temperature of formation, etc. Motivate your answer in order to get full credit. (2 p)

Pearlite:

- nucleates on grain boundaries;
- coherent with one grain → orientational relationship, and incoherent with another;
- depleted solution around nuclei → driving force for nucleation of the second phase;
- **Incoherent** interface grow
- Lamellar structure consisting of **continuous** lamellas of ferrite and cementite

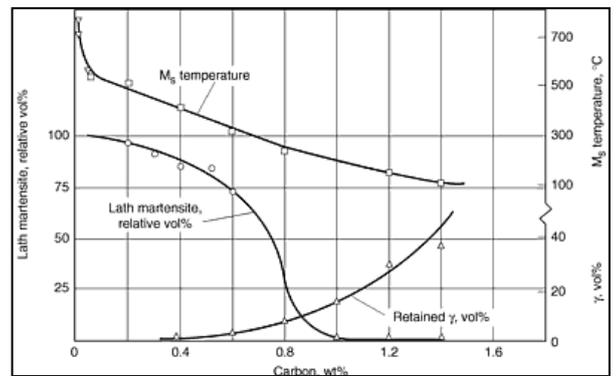
Upper bainite (350-550°C)

- needles or laths of ferrite;
- cementite precipitates between laths;
- nucleates on grain boundary, similar to Widmanstätten side-plates;
- large undercooling → low energy semicoherent interfaces;
- orientation relationship to γ -grain for ferrite and cementite (not the case for pearlite);
- **discontinuous** nature of carbides;
- finer at larger undercoolings.

6. Diffusionless transformation (3 p)

Describe two types of martensite and effect of alloying elements on its growth. Describe effect of alloying elements/martensite structure on M_s temperature and amount of residual austenite. Motivate your answer. (3p)

- Low carbon (0.4 wt.%C) low-alloyed steels - **lath martensite** - growth by nucleation dislocations at the highly-strained interface;
- **Plate martensite** – medium and high carbon, high-nickel steels - associated with lower M_s and higher amount of retained austenite;
- medium C or Ni martensite → plates with twinned central "midrib" with outer regions being free of twins;
- high C or Ni martensite is completely twinned;
- carbon content significantly effects martensite transformation temperatures (both, M_s and M_f): $M_s \sim 500^\circ\text{C}$ for low-carbon steels and considerably decreases with carbon content;
- amount of retained austenite is also considerably increases with increasing carbon content → up to 10-15% → connected to high elastic stresses between martensite plates → suppress further growth or thickening of the plates.



Metals Handbook -> Structure/Property Relationships in Irons and Steels -> Role of Microstructure

7. Novel metallic materials (2 p)

Describe shape memory effect – microstructures involved, phase transformation observed, applications. Motivate your answer to get full credit. (2 p)

Shape memory effect: material shape is deformed at a low temperature in a martensitic state and regains its shape when heated to a higher temperature and transformed to the parent phase.

- thermoelastic martensitic transformation;
- martensitic transformation in shape memory alloys is cooperative, nondiffusional, and results in a microscopic surface relief;
- martensite typically occurs as alternately sheared platelets seen as a herringbone structure metallographically;
- transformation is a first-order phase change but occur over a range of temperatures specific for each alloy system – transformation hysteresis - the transformation on heating and on cooling does not overlap.
- typical transformation vs. temperature curve for a specimen under constant load (stress) as it is cooled and heated. T , transformation hysteresis. M_s , martensite start; M_f , martensite finish; A_s , austenite start; A_f , austenite finish
- thermal shape memory effect starts from austenite that is cooled to form twinned martensite → applied stress deforms the martensite by moving twin boundaries → heating reverts the martensite to austenite “forgetting” all of the deformation attributable to moving martensite twin boundaries;
- superelasticity - in this case the martensite is stress-induced rather than thermally induced → twinned martensite condition is transitory and occurs only at the austenite-martensite interface.

8. Solid/gas interactions (3 p)

A thin sheet of iron is in contact with carburising gas on one side (carbon activity equal to 1.5 wt.%C in steel) and a decarburising gas (carbon activity equal to 0.1 wt.%C in steel) on the other side in the N_2 -2%CO-2%H₂ processing atmosphere at temperature of 1000°C. Calculate composition of the atmosphere to provide mentioned above carbon activities on the steel sheet on both sides if $K=1.184E-002$ at this temperature for the reaction $CO+H_2=C+H_2O$.

Answer:

In this case you have to make a first assumption that carbon content in the steel is equal to the carbon activity in the steel. Hence, required carbon activity has to be provided based on the chemical reaction: $CO+H_2=C+H_2O$. Equilibrium constant for this reaction is equal to $K = \frac{a_c \times P_{H_2O}}{P_{CO} \times P_{H_2}}$, where $p(CO)=0.02$ and $p(H_2)=0.02$ and so carbon activity can be adjusted by $p(H_2O)$ that is equal to: a) for 1.5 wt.%C → $p(H_2O)=3,15e-4$ bar; b) for 0.1 wt.%C → $p(H_2O)=4.74e-3$ bar.