Chalmers University of Technology
Department of Materials and Manufacturing Technology

Examination in Phase Transformations MMK162
Advanced Engineering Materials
14.00-18.00, 26 October 2012

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

Solutions and answers should be well worked out and <u>motivated</u> 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	8
2. Diffusion and solid/gas interactions	12
3. Interfaces and microstructure	5
4. Solidification of fusion welds	7
5. Diffusional transformation	11
6. Diffusionless transformation	7
Sum:	**50**

Limits for: 3>40%
                 4>60%
   5>75%

Bonus points can be used fully (8p) to pass the exam, but are only to be used to 50% (4p) for grade 4 and to 25 % (2p) for grade 5.

Göteborg, 2012.10.23

Eduard Hryha

1. Phase diagrams and free energy curves (8p)

a) Consider the Pb-Sn system according to the figure below. Draw a free energy diagram $G(X_{Sn})$ for 200°C. In the sketch mark all solid solubility limits and chemical potentials of the phase equilibriums found at this temperature. X-axis should be drawn correct compared to the phase diagram. (6)
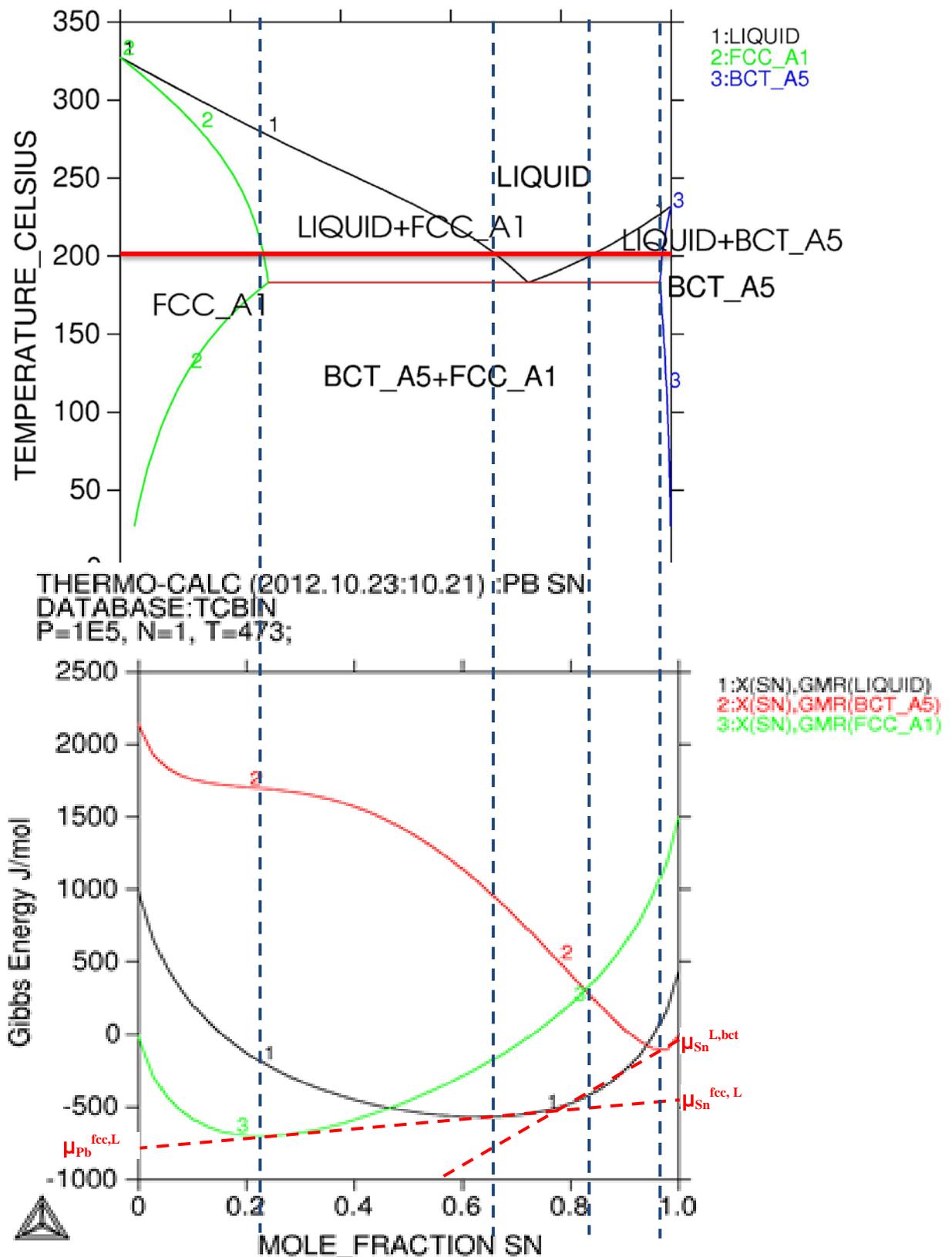
b) Sketch a schematic free energy diagram for a system, consisting of three phases α, β and γ, where α and β has different crystal structures and γ is an ordered phase. Motivation is necessary to get credit. (2)
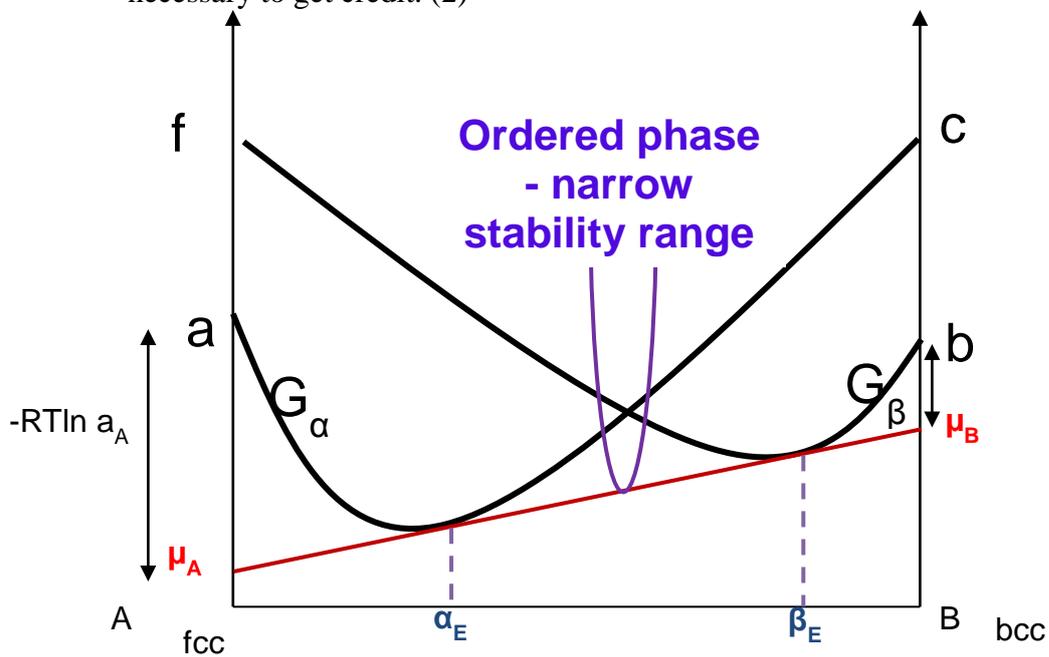

2. Diffusion and solid/gas interactions (12p)

a) Calculate and sketch concentration profile of carbon after carburization of steel at 900°C for 30 min. Carburization potential of the carburizing atmosphere is constant and equal 1%. Carbon content of the steel is 0.1%. Diffusion coefficient of carbon in austenite is $D=2.39*10^{-11}$ m^2s^{-1}. Sketch the approx. graph and table for as minimum 5 depths (5p).

C0	Cs	z	erf(z)	D	t, s	x, mm	C, %
0.1	1	0	0	2.39E-11	1800	0	1
0.1	1	0.05	0.0564	2.39E-11	1800	0.020741	0.94924
0.1	1	0.1	0.1125	2.39E-11	1800	0.041483	0.89875
0.1	1	0.5	0.5205	2.39E-11	1800	0.207413	0.53155
0.1	1	0.75	0.7112	2.39E-11	1800	0.311119	0.35992
0.1	1	1	0.8427	2.39E-11	1800	0.414825	0.24157
0.1	1	2	0.9953	2.39E-11	1800	0.829651	0.10423

$$C = C_s - (C_s - C_0) erf \frac{x}{2\sqrt{Dt}}$$

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

$$erf(0.5) = 0.5$$
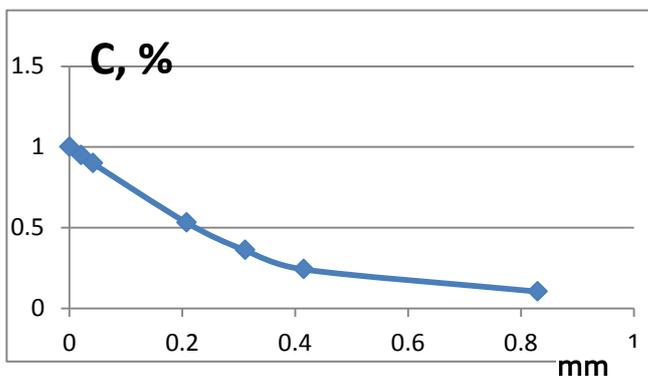
b) Define on the sketch the thickness of the carburized layer. Calculate, at the same conditions, what time is required to double the carburization depth. (2p).

$$x \approx \sqrt{Dt} \;\; \rightarrow t = \frac{x^2}{D} \rightarrow y = 2x \;\rightarrow\; t = \frac{y^2}{D} = \frac{4x^2}{D}$$

c) Carburising atmosphere is N_2-2%CO-2%H_2. Define full composition of the atmosphere (including other active gases produced by carburising reactions) to obtain required carbon activity of the atmosphere equal to 1%. K=3.531E-002 at this temperature. What other carburizing reactions can be expected in this system? (5p).

You have to find partial pressure of water vapour correcponding to required carbon activity:

$$CO + H_2 = C + H_2O$$

$$K = \frac{a_c \times P_{H_2O}}{P_{CO} \times P_{H_2}} \rightarrow P_{H_2O} = \frac{P_{CO} \times P_{H_2} \times K}{a_C} \rightarrow$$

$$P_{H_2O} = \frac{0.02 \times 0.02 \times 0.03531}{0.01} = 0.0014124$$
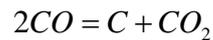
Other reactions:

$$2CO = C + CO_2$$

Table 5.3 Table of the error function

| z	erf z	z	erf z	z	erf z	z	erf z
0	0	0.40	0.4284	0.85	0.7707	1.6	0.9763
0.025	0.0282	0.45	0.4755	0.90	0.7970	1.7	0.9838
0.05	0.0564	0.50	0.5205	0.95	0.8209	1.8	0.9891
0.10	0.1125	0.55	0.5633	1.0	0.8427	1.9	0.9928
0.15	0.1680	0.60	0.6039	1.1	0.8802	2.0	0.9953
0.20	0.2227	0.65	0.6420	1.2	0.9103	2.2	0.9981
0.25	0.2763	0.70	0.6778	1.3	0.9340	2.4	0.9993
0.30	0.3286	0.75	0.7112	1.4	0.9523	2.6	0.9998
0.35	0.3794	0.80	0.7421	1.5	0.9661	2.8	0.9999

3. Interfaces and microstructure (5p)

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 what grains will grow and why. (1.5 p)
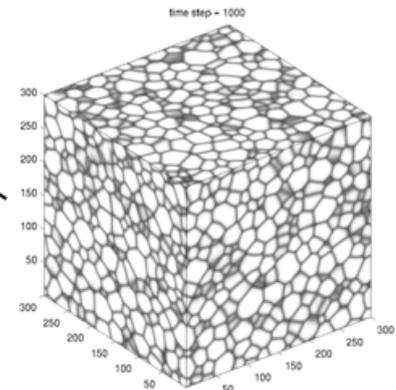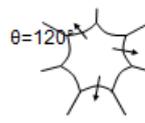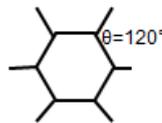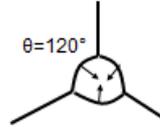

b) Explain if there are any differences in grain boundary migration during grain growth and recrystallization. Motivation is necessary to get credit. (1.5 p)

Problem 3.5:
- Grain growth – grain boundaries moves towards their centre of curvature – reduction of the total amount of GB area and so total GB energy;
- recrystallization – GB energy is insignificant in comparison with the difference in dislocation energy difference between recrystallized grain and deformed grain – boundaries can move away from their centre of curvature.

5

c) Below are four micrographs of a low-alloyed steel cooled from austenite. The micrographs present ferrite, pearlite, plate martensite and tempered lath martensite. Define which image represents which microstructure and explain why each microstructure looks as it does? Motivate your answer. (2p)

a) tempered lath martensite (carbides); b) pearlite (lammelar structure), c) plate martensite (dark plates with white untransformed austenitic areas); d) ferrite – single-phase microstructure.
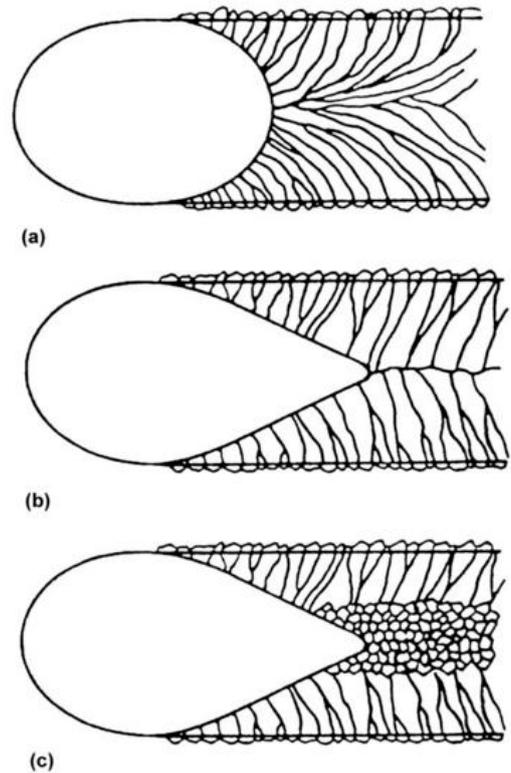

a)

b)

c)

d)
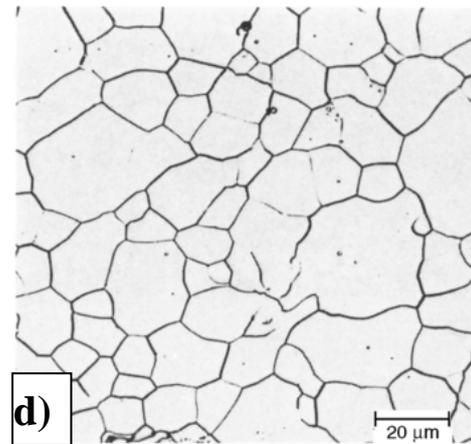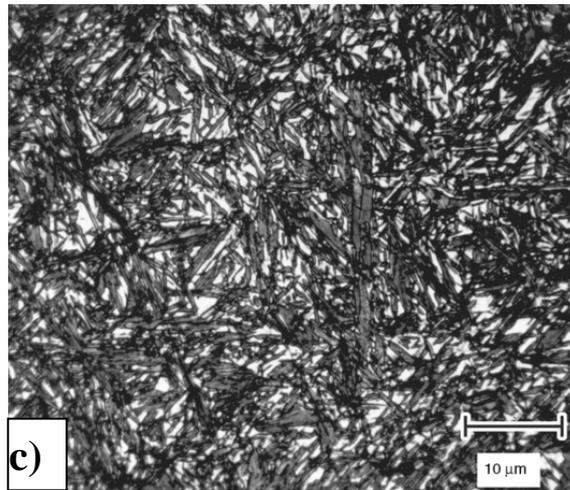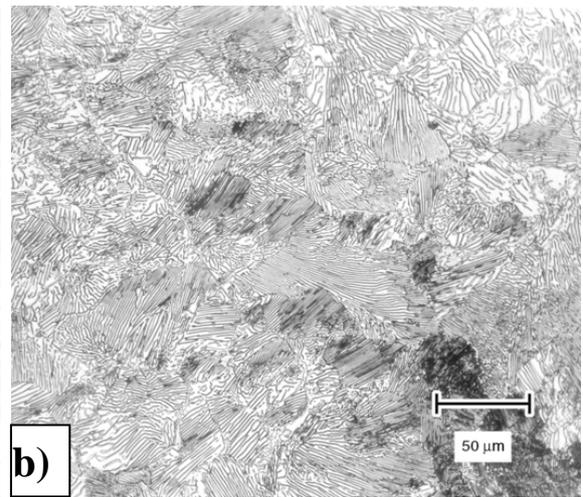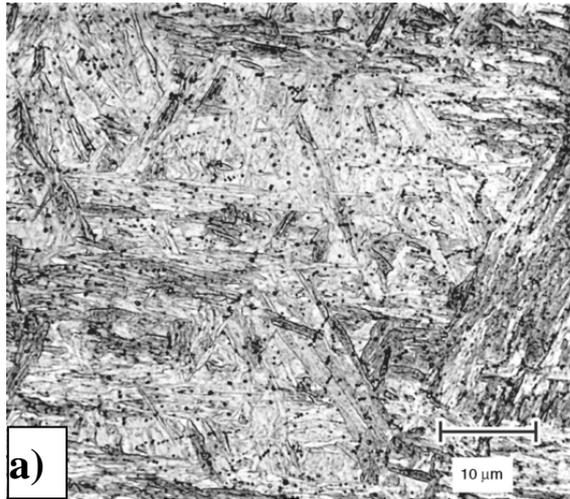
4. Solidification of fusion welds (7p)

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

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

- 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 - <100> for cubic – columnar growth;
   - no nucleation barrier;
   - determined by the grain size of the base metal.

(a)

(b)

(c)

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

b) 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. (3p)

 (a) – slowest, (c) - fastest

Welding – heat flow

Thermal conductivity (material type) effect:
- temperature spreads over a larger area and causes a larger weld pool (larger weld bead) for low-conductivity material;
- isotemperature 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 Fig 4.46
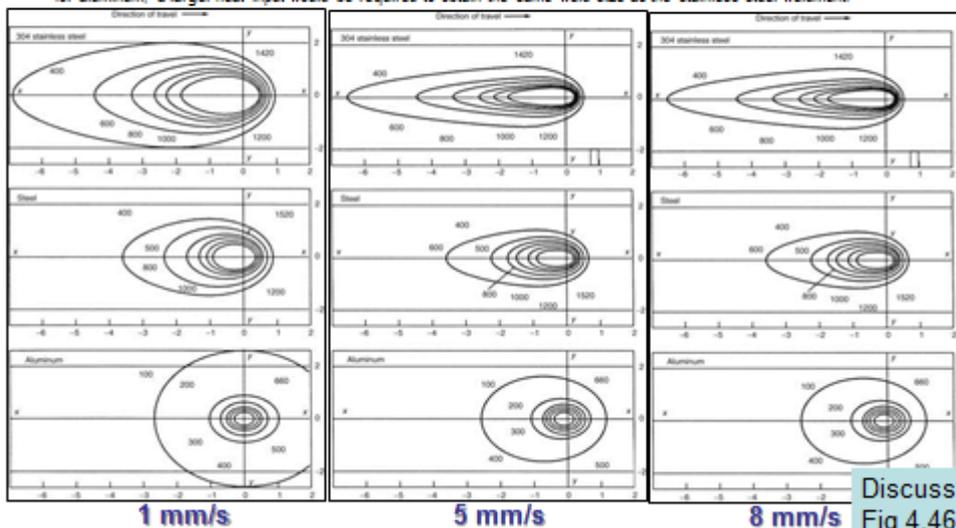
Discuss

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

c) Sketch the isotherms for all of the presented welding microstructures and based on it describe grain growth. Motivate your answer. (2p)
 –sketch isotherms as on Fig. above (pear-shaped) with description of dendrite growth as in fig. below:

## Welding - solidification microstructure
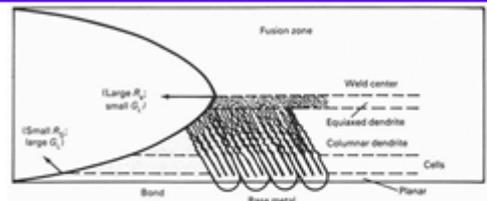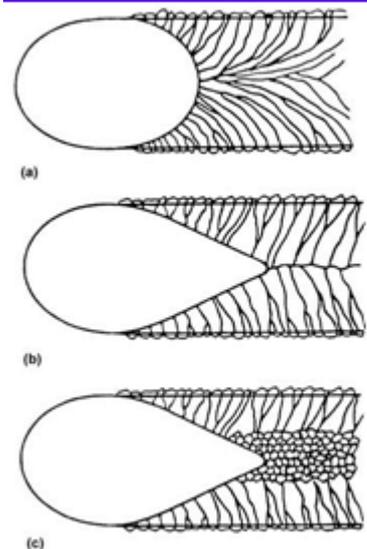
1. Epitaxial growth on melted grains of base metal
   - *same composition, low nucleation barrier*
2. Slow crystal growth, planar and then cellular
   - *Steep dT/dx stable planar interface*
3. Cellular dendritic growth in <100> direction – coarse columnar crystals
   - *dendrites perpendicular to isotherm dominates, coarsen*
4. Final solidification at centre-line, rapid growth, segregation (equiaxed)
   - *impurities, shallow dT/dx, random dendritic growth*

ASM Handbook, Volume 6A, Welding Fundamentals and Processes -> Fundamentals of Weld Solidification -> Microstructural Features in Fusion Welds

5. Diffusional transformation (11p).

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

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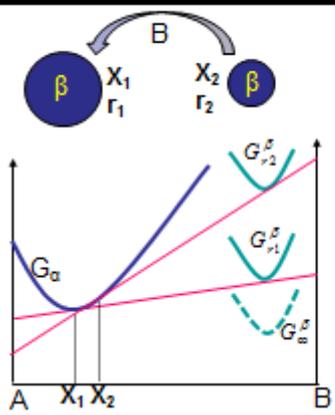
- High-density of fine precipitates tend to coarsen – decrease interfacial area – Osterwald ripening;
- Gibbs-Thomson effect: solute concentration in the matrix increases with particle size decreasing: $X_1 < X_2$;
- concentration gradient - solute diffuse to larger precipitates – coarsening of large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

$$\bar{r}^3 - r_0^3 = kt \quad ; \quad k \propto D\gamma X_e$$

- $r = r_0$ at t=0;
- X_e – equilibrium solubility of very large particle.

D and X_e increase exponentially with T, coarsening rate: $\frac{d\bar{r}}{dt} \propto \frac{k}{\bar{r}^2}$

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

Stabilization of fine precipitates:		
Low γ: interfacial energy;	D: diffusion coefficient;	X_e: equilibrium solubility of r=∞

- 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.

c) Below are presented TTT and CCT diagrams for the 5140 steel. Describe the difference between two types of diagrams presented. Motivate your answer. (1p)

-time-temperature-transformation diagrams (TTT) – has nose shape – correlation between the nucleation and diffusion;
- continuous-cooling-transformation diagrams (CCT);

d) Show how you will perform your cooling to obtain:
   a. 100% pearlitic structure (1 p) – *impossible to obtain pearlite without ferrite, but cooling with rate <0.08 C/s can be used to get pearlite;*
   b. ~50% of upper bainite (1 p) – *cooling with rate in the range 2 to 8 C/s, but difficult to control. Another way by quenching to ~500 C and tempering at this temperature*
   c. fully martensitic structure (1 p) – *cooling with rate ≥100C/s;*
   d. if 50% bainite is going to be formed, what will be the rest? (1 p) – *ferrite/pearlite if cooling rate between approx. 1 and 10 C/s is applied and martensite if cooling rates between 10 and 100 C/s are applied;*
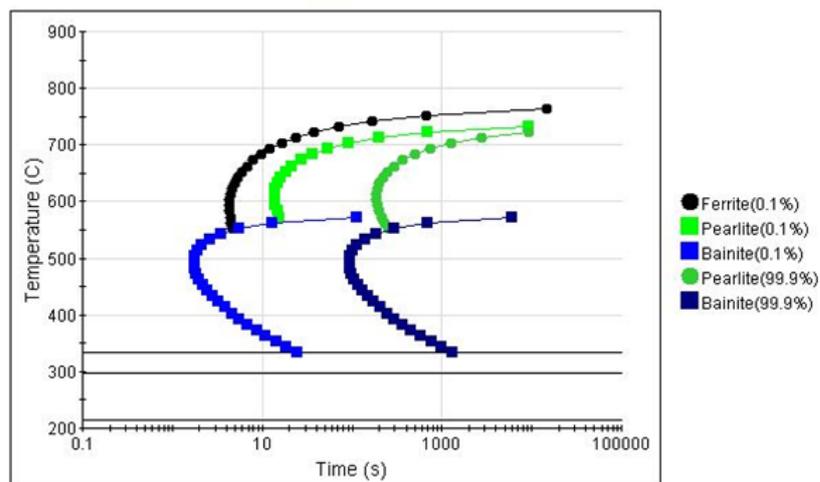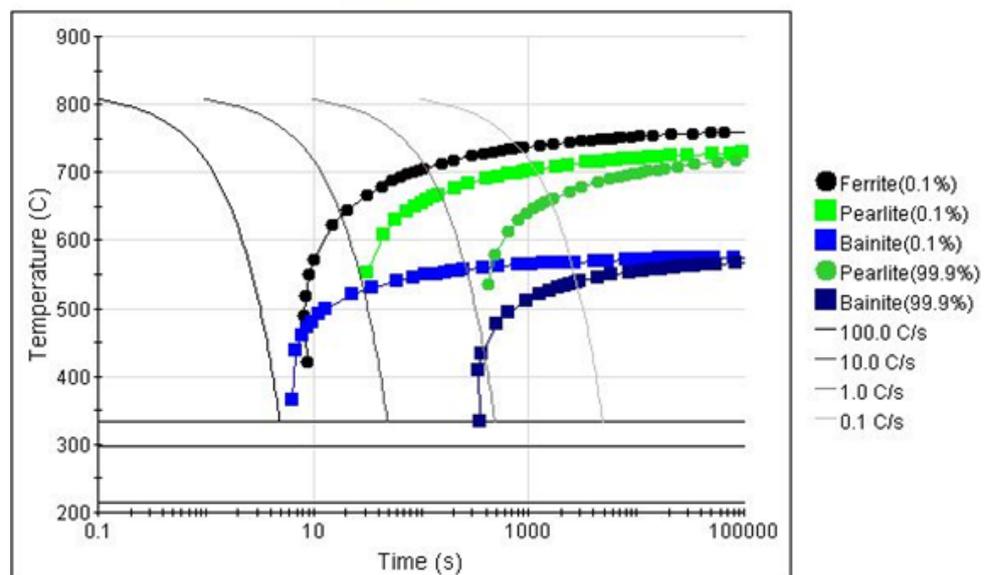
6. Diffusionless transformation (7p)

Martensite is form from austenite at large undercooling by diffusionless transformation, or so called military transformation.

a) Describe the most likely mechanism of martensite nucleation during cooling. Motivate your answer. (2p).

Martensite nucleation – heterogeneous

Dislocations – heterogeneous sites of martensite nucleation:
Nucleation on dislocation core:
- **Zenner**: movement of partial dislocation during twinning could generate thin **bcc** region:
  - produce nuclei only two atomic layers thick...
- **Venables**: martensite forms via intermediate epsilon martensite: $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$:
  - no evidence of $\varepsilon' \rightarrow \alpha'$ transformation;
  - ε' and α' form independently.

Disslocation strain energy assisted deformation:
- strain field associated with disslocation provide favourable interaction with the strain field of nucleus:

$$\Delta G = -V\Delta G_v + A\gamma + V\Delta G_{Strain} - \Delta G_{dislocation}$$

$$\Delta G_d = 2\mu s \pi a c b \leftarrow \text{Dislocation interaction energy – reduces the nucleation energy barrier!}$$

- fully coherent nucleus can reach a size of ~20 nm in diameter and 2-3 atomic layers thick;
- for further growth → slip or twin is needed to further reduce strain energy.

b) Describe two types of martensite and effect of alloying elements on its nucleation/growth. Motivate your answer. (3p)

Austenite and ferrite stabilizing alloying elements – both lower transformation temperature:
Andrews equation: $\mathbf{M_s(°C) = 539 - 423(C) - 30.4(Mn) - 12.1(Cr) - 17.7(Ni) - 7.5(Mo)}$

Lath martensite - low carbon (0.4 wt.%C) low-alloyed steels:
- growth by nucleation dislocations at the highly-strained interface → misfit energy reduced and lath is able to continue growing;
- limited diffusion of carbon take place following/during transformation → connected to higher M_s temperature associated with lath martensite;
- low amount of residual austenite – sideway growth and transformation between laths is not probable to occur.

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;
- growth mechanism is unclear.

c) What is the role of austenitic grain size in martensitic transformation? Is the austenitic grain size important to the final strength of martensite? Motivate your answer. (2p)

High-angle grain boundaries – effective barrier to grain growth;
- grain size do not effect the volume concentration of nucleation sites BUT martensite plate size is a function of a grain size: large grain size → large built-up of strains associated with transformation between adjacents grains → grain-boundary rupture (quench cracking). Fine grain size → "self-accomodating" → stronger and tougher material.