

Chalmers University of Technology
Department of Materials and Manufacturing Technology

Examination in Phase Transformations MMK162
Advanced Engineering Materials
13.00-17.00, 30 October 2015

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	12
2. Diffusion	8
3. Interfaces and microstructure	9
4. Solidification	8
5. Diffusional transformations	7
6. Diffusionless transformations	4
7. Solid/gas interactions	2
Sum:	50

Limits for: 3>45% (22.5 – 30)
 4>60% (30.5 – 40)
 5>80% (40.5 – 50)

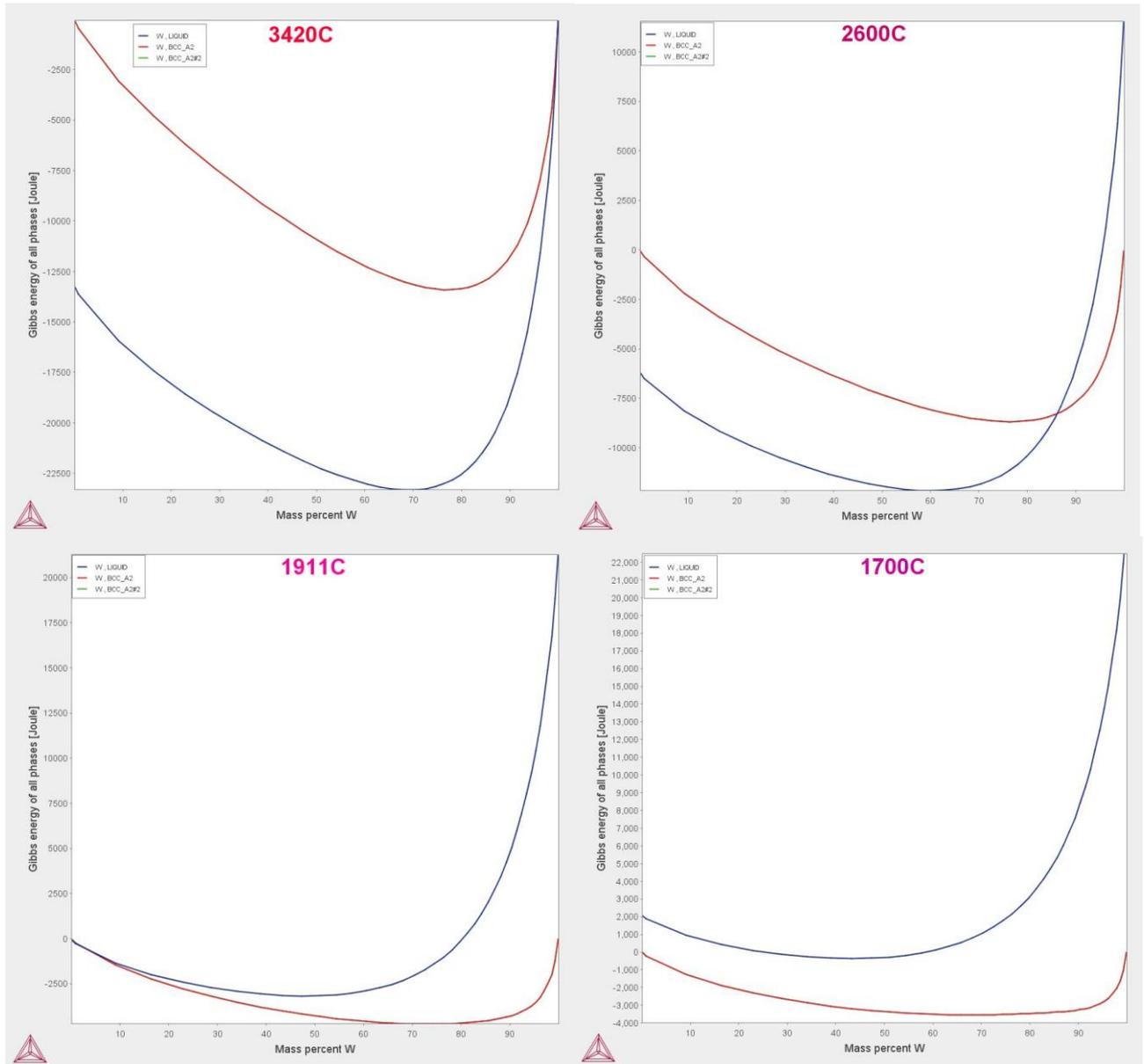
Grading will be based on the total sum of **50 points**. Bonus points earned during lectures (quiz) will be added to the exam points.

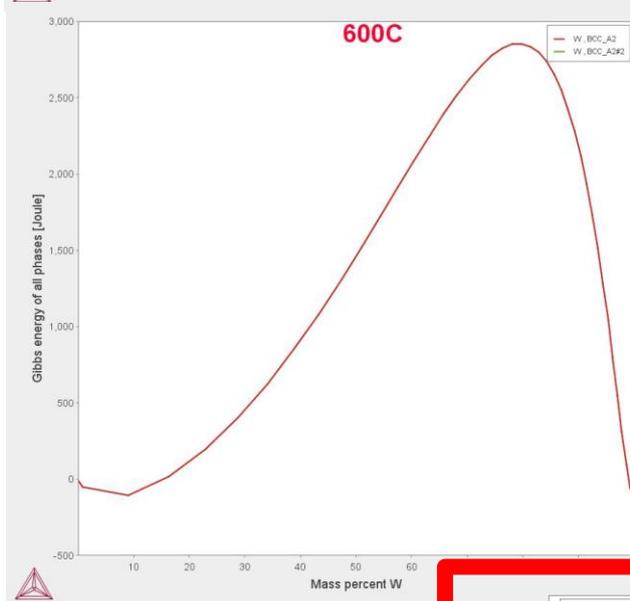
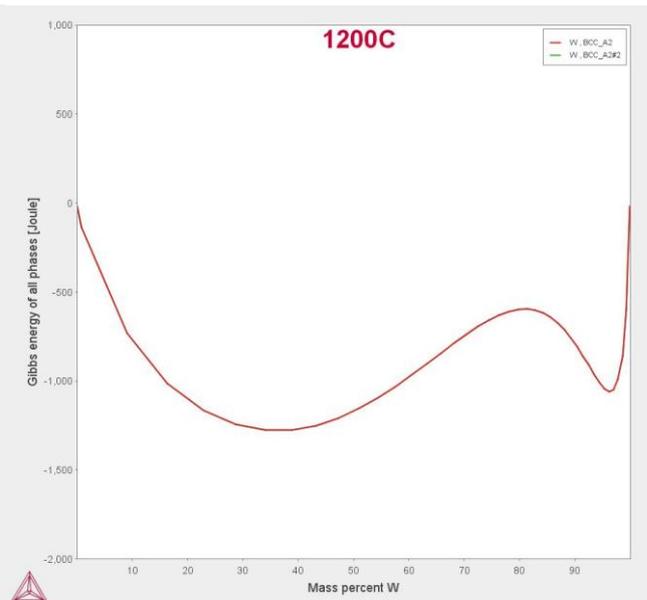
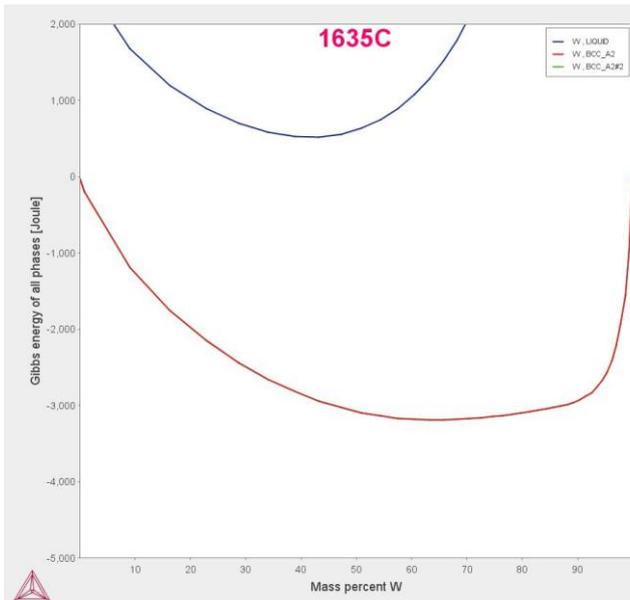
Göteborg, 2015.10.28

Assoc. Prof. Eduard Hryha

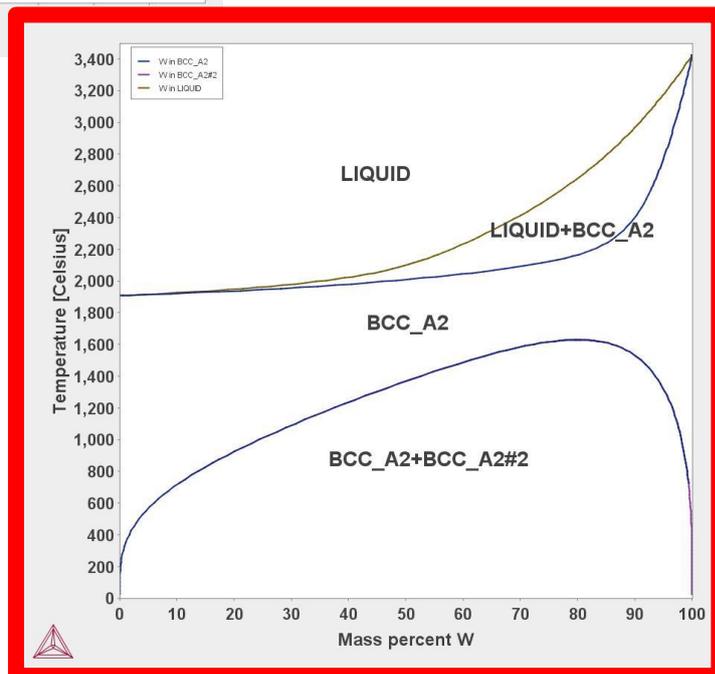
1. Phase diagrams and free energy curves (12 p)

- a) Derive phase diagram for Cr-W system using free energy diagrams according to the figure below. Respective temperatures are 3420, 2600, 1911, 1700, 1635, 1200 and 600 °C (marked on the top of each figure). X and Y-axes should be drawn in correct scale compared to the phase diagram. Mark phases in the respective phase stability fields on the diagram (5).
- b) Mark chemical potentials of the phase equilibria for the free energy diagram at 2600°C. (1 p)

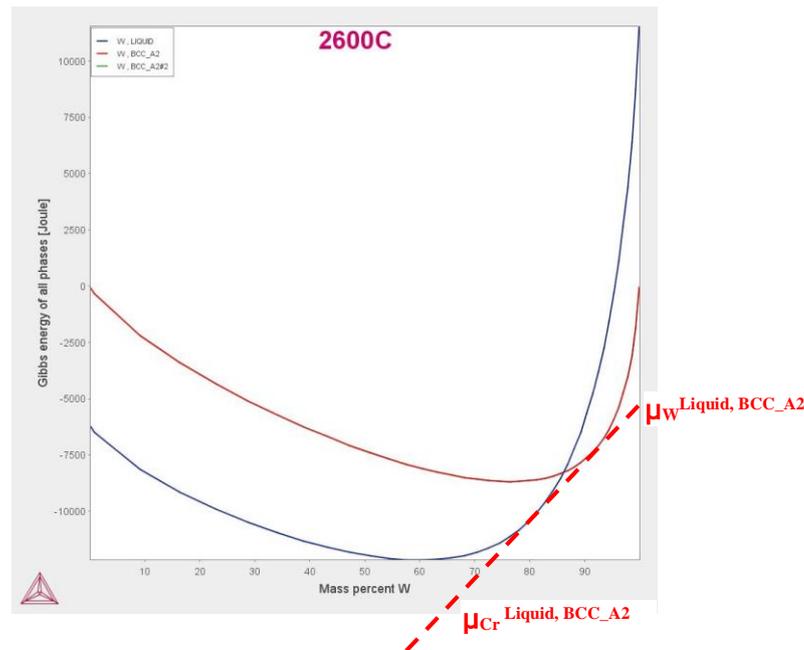




a) Answer:



b)



- c) How similar is crystallographic structure of the Cr-rich BCC_A2 and W-rich BCC_A2#2? How is that reflected on G-curve? Short motivation is necessary to get full credit. (1 p)

Cr-rich BCC_A2 and W-rich BCC_A2#2 have the same BCC structure with only difference in lattice parameter (hence, marked as BCC_A2 and BCC_A2#2) – this results in the common G-curve for both. In case elements A and B have different crystallographic structures – each structure will have its own G-curves and so two separate G-curves will be present on the graphs above.

- d) Describe the differences between ideal and regular solid solutions based on the Gibbs free energy – describe differences between the entropy and enthalpy of the ideal and regular solid solutions. Describe physical meaning of the enthalpy and entropy for both cases and express it using representative mathematical equations. Motivation is necessary to get full credit. (3 p).

In case of ideal solid solutions, the free energy change on mixing is connected only to the change in entropy as there is no heat of mixing ($\Delta H_{mix} = 0$) and so: $G_2 = X_A G_A + X_B G_B + \Delta G_{mix}$ where $\Delta G_{mix} = -T\Delta S_{mix}$. Entropy has two contributions: configurational and thermal: $S = k_B \ln \omega$; $S = S_{th} + S_{config}$; ω_{th} : No of ways thermal energy can be divided among atoms = number of ways vibration can be set up (here: no change in heat or volume – no change in ω_{th}); ω_{conf} : number of ways arranging atoms in a solution. Hence, $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = -T(S_2 - S_1) = -T(k_B \ln \omega_{config2} - k_B \ln \omega_{config1}) = -T(k_B \ln \omega_{config2} - k_B \ln 1) = -T k_B \ln \omega_{config2}$

Using statistical approach it can be shown that for ideal solution:

$$\Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B)$$

Because $X_{A,B} < 1$ this means that $\Delta S_{mix} > 0 \rightarrow$ entropy always increase on mixing and so $\Delta G_{mix} < 0 \rightarrow$ free energy decrease on mixing. So Gibbs free energy:

$$G_2 = G_1 + \Delta G_{mix} = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)$$

In case of regular solutions, heat of mixing has to be taken into account: $\Delta H_{mix} \neq 0$:

- $\Delta H_{mix} > 0 \rightarrow$ endothermic \rightarrow heat absorbed
- $\Delta H_{mix} < 0 \rightarrow$ exothermic \rightarrow heat evolved

Quasi-chemical approach:

- ΔH_{mix} (ΔE) determined by bonds energies between adjacent atoms only;
 - volumes of pure A and B are equal and not changed during mixing ($V=const.$);
- \rightarrow inter-atomic distances and bond energies are independent of composition

Energy of the bonds:

1. A-A bonds each with energy ϵ_{AA}
2. B-B bonds each with energy ϵ_{BB}
3. A-B bonds each with energy ϵ_{AB}

$\epsilon=0$ – state where the atoms are separated to infinity $\rightarrow \epsilon$ is negative, stronger bond \rightarrow more negative

Number and type of bonds determine the internal energy of the solution:

$$E = P_{AA}\epsilon_{AA} + P_{BB}\epsilon_{BB} + P_{AB}\epsilon_{AB}$$

Number of bonds per atom:

$$P_{AB} = N_a z X_A X_B$$

If $\epsilon < 0 \rightarrow$ atoms will prefer to be surrounded by atoms of the opposite type $\rightarrow P_{AB}$ increase;
 If $\epsilon > 0 \rightarrow$ atoms will prefer to be surrounded by atoms of the same type $\rightarrow P_{AB}$ is less than in random solution;

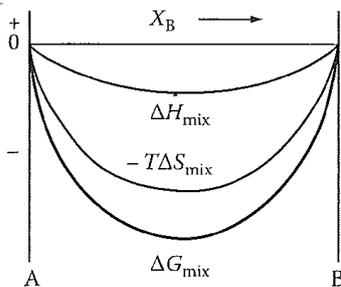
$$\Delta H_{mix} = P_{AB}\epsilon = \epsilon N_a z X_A X_B \text{ or expressed as } \Delta H_{mix} = \Omega X_A X_B \text{ where } \Omega = \epsilon N_a z$$

$$\Delta G_{mix} = N_a z \epsilon X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

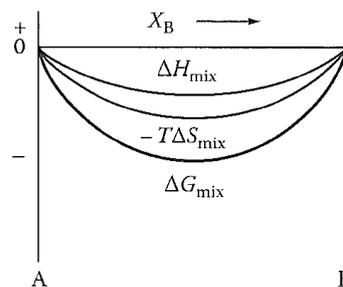
$$G = G_1 + \Delta H_{mix} - T\Delta S_{mix} = G_A X_A + G_B X_B + N_a z \epsilon X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

- e) Draw schematic diagrams of the effect of the exothermic and endothermic enthalpies of mixing in combination with temperature (low and high) on the shape of the curve of the free energy change on mixing ΔG_{mix} . Describe effect of concentration of solute on ΔG_{mix} in all cases. Short motivation is necessary to get full credit. (2 p).

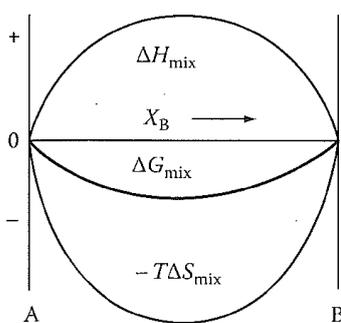
Answer:



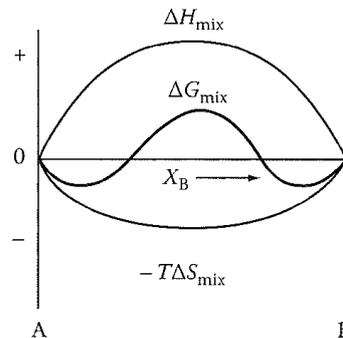
(a) $\Omega < 0$, high T



(b) $\Omega < 0$, low T



(c) $\Omega > 0$, high T



(d) $\Omega > 0$, low T

In all cases when X_A or $X_B \rightarrow 0$ - - $T\Delta S_{mix}$ becomes vertical but slope of $\Delta H_{mix} \rightarrow \Omega$. Hence, except at absolute zero, ΔG_{mix} always decrease on addition of small amount of solute.

2. Diffusion (8 p)

- a) Calculate and sketch concentration profile of carbon after exposure of the steel at the oxidizing conditions (decarburization) at 1000°C for 30 min. Carbon potential of the processing atmosphere is constant and equal to 0.05%. Carbon content of the steel is 0.8%. Diffusion coefficient of carbon in austenite is $D=4 \cdot 10^{-11} \text{ m}^2\text{s}^{-1}$. Calculate values of the carbon content for as minimum 5 depths and based on it sketch approximate graph of carbon profile. (5p).

Table 5.3 Table of the error function

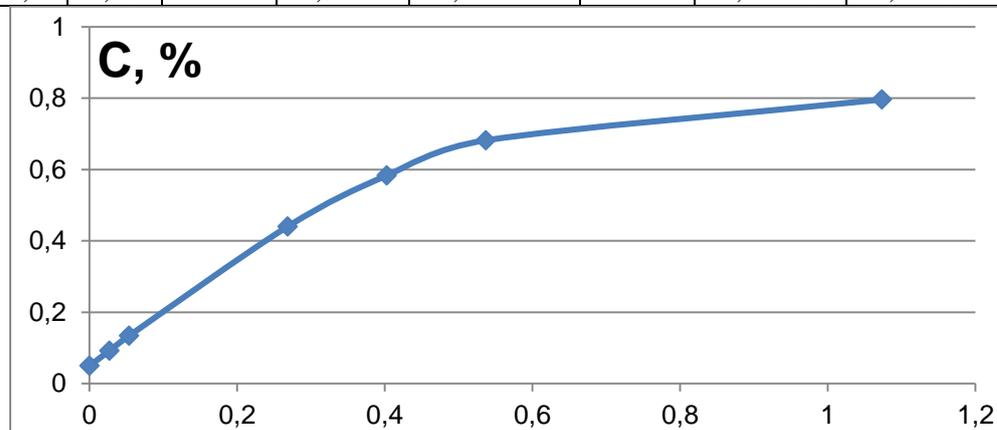
z	$\text{erf } z$	z	$\text{erf } z$	z	$\text{erf } z$	z	$\text{erf } z$
0	0	0.40	0.4284	0.85	0.7707	1.6	0.9763
0.025	0.0282	0.45	0.4755	0.90	0.7970	1.7	0.9838
0.05	0.0564	0.50	0.5205	0.95	0.8209	1.8	0.9891
0.10	0.1125	0.55	0.5633	1.0	0.8427	1.9	0.9928
0.15	0.1680	0.60	0.6039	1.1	0.8802	2.0	0.9953
0.20	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

Carbon profile in case of decarburization: $C = C_0 \text{erf} \frac{x}{2\sqrt{Dt}}$ is valid only in case when carbon potential of the processing gas is equal to $C_s=0!!!$

However, in case you have defined carbon potential of the atmosphere (0.05 %C) – you have to use the same equation as for carburization $C = C_s - (C_s - C_0) \text{erf} \frac{x}{2\sqrt{Dt}}$ where $C_s=0.05\% \text{C}$ and

$C_0=0.8\% \text{C}$. To simplify calculations it is easier to choose values of z and respective values of $\text{erf}(z)$ from table of values of error function. Then, by knowing the value of z and Dt you can calculate depth x . By knowing the value of $\text{erf}(z)$ you can calculate C . The sketch of carbon profile is presented below the table.

C_0	C_s	z	erf	D	$t, \text{ s}$	Dt	$2\text{sqrt}(Dt)$	C	$x \text{ (mm)}$
0,8	0,05	0	0	4,00E-11	1800	7,2E-08	0,000537	0,05	0
0,8	0,05	0,05	0,0564	4,00E-11	1800	7,2E-08	0,000537	0,0923	0,026833
0,8	0,05	0,1	0,1125	4,00E-11	1800	7,2E-08	0,000537	0,134375	0,053666
0,8	0,05	0,5	0,5205	4,00E-11	1800	7,2E-08	0,000537	0,440375	0,268328
0,8	0,05	0,75	0,7112	4,00E-11	1800	7,2E-08	0,000537	0,5834	0,402492
0,8	0,05	1	0,8427	4,00E-11	1800	7,2E-08	0,000537	0,682025	0,536656
0,8	0,05	2	0,9953	4,00E-11	1800	7,2E-08	0,000537	0,796475	1,073313



- b) Describe diffusion in substitutional alloys – namely, describe Fick’s first and second law in case of substitutional diffusion, as well as first and second Darkens’ 1-st and 2-nd equations. Describe the meaning of the interdiffusion coefficient and its experimental determination. Motivation and presentation of respective equations is required to obtain full credit. (2 p)

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Diffusion in substitutional alloys

A thin slice δx at a fixed distance x from the end of the couple (outside diffusion zone):

$$\frac{\partial C_A}{\partial t} = -\frac{\partial J'_A}{\partial x}$$

Total flux of A atoms dJ'_A across stationary plain with respect to the specimen has two components: 1) diffusive flux relative to lattice; 2) flux vC_A due to velocity of lattice

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

$$J'_A = -D_A \frac{\partial C_A}{\partial x} + vC_A$$

Where:
 $X_A = C_A/C_0$
 $X_B = C_B/C_0$

$$J'_A = -(X_B D_A + X_A D_B) \frac{\partial C_A}{\partial x}$$

$$J'_A = -\tilde{D} \frac{\partial C_A}{\partial x}$$

Fick's 1st law

$$\tilde{D} = X_B D_A + X_A D_B$$

interdiffusion coefficient

$$J'_A = -J'_B$$

$$J'_B = \tilde{D} \frac{\partial C_A}{\partial x}$$

Darken 2-nd eq.

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\tilde{D} \frac{\partial C_A}{\partial x} \right)$$

Fick's 2d law

Fig 2.21

Eduard Hryha Diffusion 33

Darken 1-st eq

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

\tilde{D} is experimentally determined with diffusion pairs

If D_A and D_B are to be determined separately, the rate of lattice movement, v , must be known. If cavities (vacancies/pores) are formed instead of movement of lattice planes, the resulting equations become complicated – almost impossible to evaluate interdiffusion coefficient.

- c) Describe Kirkendall effect and its physical principle on example of Cu-Zn brass (schematically). Which types of defects can be created in the materials due to the Kirkendall effect? Motivation is required to obtain full credit. (1 p)

Kirkendall effect: Displacement of inert wires – α -brass (Cu-30%Zn) wound by Mo-wires in pure Cu. High difference in the diffusion coefficients between two elements in the alloy can result in the **creation of holes or voids (Kirkendall porosity)** as the vacancies can be absorbed by internal boundaries, surfaces, inclusions, etc.

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Diffusion in substitutional alloys

Kirkendall effect (1947!): after annealing separation between wires (w) decreases \rightarrow difference in $D: D_{Zn} > D_{Cu}$

Cu (high concentration)

Marker Motion

High Zn Conc. Brass (Cu+Zn)

Mo wires

Source: Wikipedia

Eduard Hryha Diffusion 35

3. Interfaces and microstructure (9p)

a) Describe the main differences between the low-, high- and special-angle grain boundaries, their surface energy and mobility. (2 p).

- Low angle grain boundary - misorientation between two grains small \rightarrow array of dislocations. Energy of boundary is equal to the total energy of dislocations within unit area of boundary.

- Energy of boundary depends on the spacing of dislocations $D \rightarrow D = \frac{b}{\sin\theta} \approx \frac{b}{\theta}$

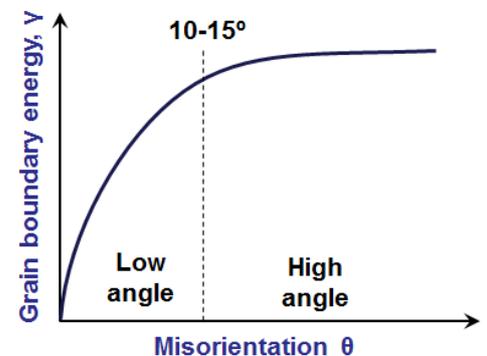
- At very small θ , γ is proportional to the dislocation density in the boundary: $\gamma_b \propto \frac{1}{D} \propto \theta$

- As θ increases \rightarrow strain field of dislocations progressively cancel $\rightarrow \gamma$ increases at decreasing rate;

- at $\theta > 10-15^\circ$ - dislocation cores overlap \rightarrow impossible to identify individual dislocations $\rightarrow \gamma_b$ is almost independent on θ .

- At $\theta > 10-15^\circ \rightarrow$ **random high angle boundary** \rightarrow poor fit, relatively open structure, bonds between atoms are broken or highly distorted \rightarrow high γ_b , γ_b is almost independent of θ :

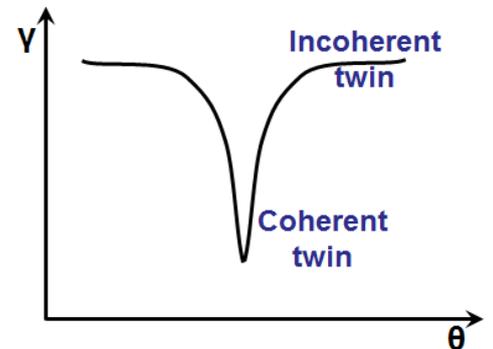
- Measured high-angle GB energies, γ_b , are often found to be $\gamma_b \approx \frac{1}{3} \gamma_{sv}$;



Special High-Angle Grain Boundaries \rightarrow have lower energy than random high-angle grain boundaries \rightarrow particular misorientations allowing good fit between adjoining lattices. Example is coherent twin boundary, for example in fcc at $\theta = 70.5^\circ$ around $\langle 110 \rangle$. Energy of twin boundary is very sensitive to orientation \rightarrow if twin boundary does not lie exactly parallel to the twinning plane – incoherent twin boundary:

- Random high angle boundary – open structure and so high mobility than low-angle or special high-angle grain boundaries;

- Special high angle boundary – low mobility but *can* have higher mobility than random if impurities stick to random high angle boundaries!



b) Explain thermodynamic basics of the grain boundary migration, namely: driving force, activation energy and its effect on the net flux of atoms. Describe term “mobility” of the grain boundary and its connection to the driving force. Presentation of the relevant equations, sketch of the Gibbs free energy curve (with marked driving force and activation energy barrier) as well as motivation of the answer are necessary to get full credit. (3 p).

Answer:

At sufficiently high temperature ($T > 0.5 T_m$) GB will migrate in order to reduce G . **Slides:**

Thermally Activated Migration of Grain Boundaries

Surface tension must also be balanced → $\Delta P = \frac{2\gamma}{r}$ $dG = -SdT + VdP$
 ΔP caused by curved boundary: $T = \text{const}$
 $dG = VdP$

- Pressure difference due to the curvature of the boundary creates difference in free energy or chemical potential (identical in pure metal):
 - $\Delta G \rightarrow$ force pulling GB towards grain with higher free energy

Grain boundary moves $\delta x \rightarrow$ amount of material (mol) transported over GB is $\delta x \cdot l/V_m$ and so energy decrease ΔG (per mol): $\Delta G \frac{\delta x}{V_m} = F \delta x$

Pulling force per unit area of the grain boundary: $F = \frac{\Delta G}{V_m}$

Pulling force on the boundary F is the free energy difference per unit volume

Thermally Activated Migration of Grain Boundaries

In order for an atom to move from grain 1 to grain 2 it has to acquire, by thermal activation, activation energy ΔG^a :

J Net flux of atoms (grain 1 \rightarrow grain 2): vibration/jump frequency ν ; activation energy ΔG^a ; no. atom/unit area, n_i ; probability to stick A :

$J_{12} = A_2 n_1 \nu_1 \exp\left(-\frac{\Delta G^a}{RT}\right)$

Similar flux in reverse direction (grain 2 \rightarrow grain 1) \rightarrow but atom in grain 2 has lower free energy by ΔG (per mol): $J_{21} = A_1 n_2 \nu_2 \exp\left(-\frac{\Delta G^a + \Delta G}{RT}\right)$

$\Delta G = 0 \rightarrow$ grains are in equilibrium: $A_1 n_2 \nu_2 = A_2 n_1 \nu_1$ For high-angle grain boundaries \rightarrow accommodation factors are ~ 1 $A_1 \approx A_2 \approx 1$

Thermally Activated Migration of Grain Boundaries

Assuming that even for small $\Delta G \rightarrow A_1 \approx A_2 \approx 1 \rightarrow$ net flux of atoms (grain 1 \rightarrow grain 2):

$J_{net} = A_2 n_1 \nu_1 \exp\left(-\frac{\Delta G^a}{RT}\right) \left\{ 1 - \exp\left(-\frac{\Delta G}{RT}\right) \right\}$

In typical cases $\Delta G \ll RT$, velocity of the GB movement: $v = \left[\frac{A_2 n_1 \nu_1 V_m^2}{N_a RT} \exp\left(-\frac{\Delta G^a}{RT}\right) \right] \frac{\Delta G}{V_m}$ $\frac{\Delta G}{V_m}$ - Driving force

M- mobility

Velocity of boundary movement v should be proportional to the driving force $\Delta G/V_m$ so: $v = M \frac{\Delta G}{V_m}$

M- mobility- velocity of the boundary under unit driving force: $M = \left[\frac{A_2 n_1 \nu_1 V_m^2}{N_a RT} \exp\left(\frac{\Delta S^a}{R}\right) \right] \exp\left(-\frac{\Delta H^a}{RT}\right)$

- Mobility exponentially increase with temperature;
- Compare with boundary diffusion: diffusion involves transport along the boundary \rightarrow migration requires atomic movement across the boundary.

c) Describe mobility of the different types of grain boundaries and effect of the segregation on them. Describe effect of the temperature and solubility on segregation. Presentation of the relevant equations as well as motivation of the answer are necessary to get full credit. (1 p).

- Random high angle boundary – open, high mobility
- Special high angle boundary – low mobility but can have higher mobility than random. The reason for this is that impurities stick to random high angle boundaries and so decrease their mobility.
- Decreased solid solubility in the matrix: further lowered mobility due to increased grain

$$X_b \cong X_0 \exp \frac{\Delta G_b}{RT}$$

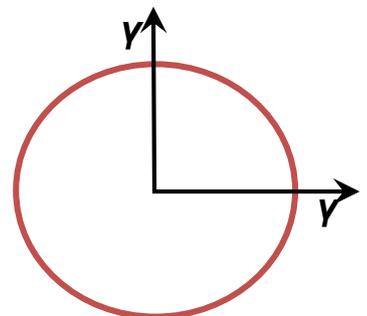
boundary concentration, X_b

Free energy released when a solute atom is moved from the matrix to the grain boundary, ΔG_b :

- ΔG_b is usually positive and increases with increasing of misfit between the solute and the matrix;
- Grain boundary segregation decreases as temperature increases – “evaporation” of the solute into the matrix;
- For low temperatures and high $\Delta G_b \rightarrow X_b$ approaches unity – maximum saturation value;
- Boundary mobility varies markedly between elements – segregation increases as the matrix solubility decreases;
- Solute atoms exert drag on the boundary that reduces boundary velocity;
- ΔG_b measures tendency of segregation.

d) Describe the shape of the fully coherent precipitates based on interface energy. Describe the effect of the misfit and matrix properties (isotropic or anisotropic) on the shape of the fully coherent precipitates. Presentation of the relevant equations as well as motivation of the answer are necessary to get full credit. (3 p).

- When β phase precipitates in α matrix \rightarrow system will have minimum free energy when precipitate shape and orientation to matrix is optimized to give lowest interfacial energy
- If precipitate β has the same crystal structure as α matrix and similar lattice parameter \rightarrow two phases can form low energy coherent interfaces \rightarrow formation of fully coherent precipitates or GP zones (Guinier-Preston)
- Two crystal structures match almost perfect across all interfacial planes \rightarrow no large misfit or strain \rightarrow isotropy in γ \rightarrow equilibrium shape should be a sphere
- However, presence of misfit raises free energy of a system connected to elastic strain ΔG_s , than conditions for equilibrium (see slide below)



Second-Phase Shape: Misfit Strain Effects

- Fully Coherent Precipitates

Presence of misfit raises free energy of a system connected to elastic strain ΔG_s , than conditions for equilibrium:

$$\sum_i A_i \gamma_i + \Delta G_s = \min$$

a_α and a_β → lattice parameters of unstrained matrix and precipitate → unconstrained misfit δ :

$$\delta = \frac{a_\beta - a_\alpha}{a_\alpha}$$

Stresses maintaining coherency distort precipitate lattice → increase of spherical precipitate distortion is uniform in all directions → new lattice parameter a_β' . In-situ or constrained misfit ϵ :

$$\epsilon = \frac{a_\beta' - a_\alpha}{a_\alpha}$$

If elastic moduli of the matrix and inclusion are equal and Poisson's ratio is 1/3:

$$\epsilon = \frac{2}{3} \delta$$

Different elastic moduli:

$$0.5\delta < \epsilon < \delta$$

If matrix is elastically isotropic and the same elastic moduli and elastic strain energy is shape independent → particle a sphere:

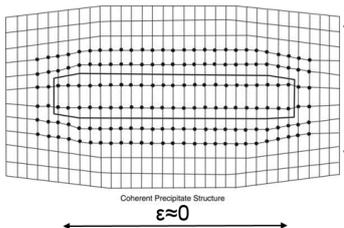
$$\Delta G_s \approx 4\mu\delta^2 \cdot V$$

μ - shear modulus
 V - volume of particle
 δ - lattice misfit

Coherency strains produce an elastic strain energy, proportional to $V_{(precipitate)}$ and increasing as δ^2 .

Second-Phase Shape: Misfit Strain Effects

- Fully Coherent Precipitates



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

Different elastic moduli:

- hard inclusion - **sphere**
- soft inclusion - **disc**
- Anisotropy in matrix:
 - **disc**

Most cubic metals are elastically anisotropic: soft in $\langle 100 \rangle$ direction and hard in $\langle 111 \rangle$ direction → equilibrium shape is disc, parallel to $\{100\}$

Misfit < 5% - interface energy effects important - **sphere**
 Misfit > 5% - coherency strain energy important - **disc**

Atom radius A	Al: 1.43	Ag: 1.44	Zn: 1.38	Cu: 1.28
Zone misfit δ				
Zone shape				

4. Solidification (8 p)

- a) Describe homogeneous nucleation in solids, namely: driving force, change in the Gibbs free energy of the system due to the formation of the small sphere of solid, difference between the cluster and nuclei as well as rate of the homogeneous nucleation. Estimate the rate of the critical undercooling and present graphical relationship between the maximum cluster size and critical nuclei size. Presentation of the relevant equations, sketch of the Gibbs free energy curves and curve for the rate of homogeneous nucleation as well as motivation of the answer are necessary to get full credit. (3 p).

Driving force for solidification: $\Delta G_v \approx \Delta H - T\Delta S = L - T \frac{L}{T_m} = \frac{L \cdot (T_m - T)}{T_m} = \frac{L \cdot \Delta T}{T_m}$

Consider liquid at a temperature ΔT below T_m with a free energy G_1 :

$$G_1 = (V_s + V_L)G_v^L$$

If some atoms of liquid cluster together to form a small sphere of solid:

$$G_2 = V_s G_v^S + V_L G_v^L + A_{SL} \cdot \gamma_{SL}$$

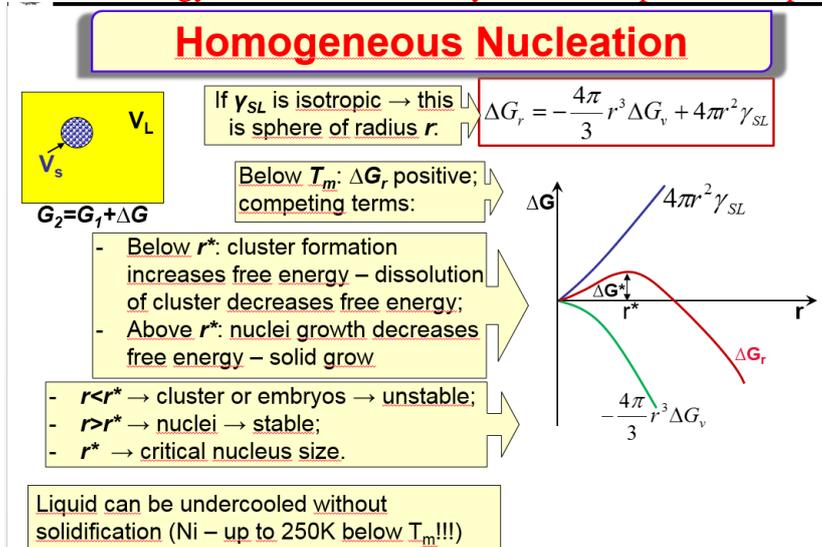
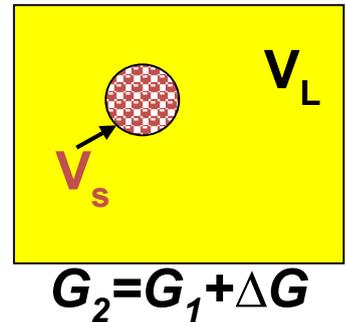
Formation of solid results in free energy change ΔG :

$$\begin{aligned} \Delta G &= G_2 - G_1 = V_s G_v^S + V_L G_v^L + A_{SL} \cdot \gamma_{SL} - (V_s + V_L)G_v^L = \\ &= -V_s(G_v^L - G_v^S) + A_{SL} \cdot \gamma_{SL} = -V_s \Delta G_v + A_{SL} \cdot \gamma_{SL} \end{aligned}$$

Below $T_m \rightarrow \Delta G_v$ is **positive** so that creation of solid has negative contribution to ΔG ;

Creation of solid/liquid interface – positive contribution to ΔG .

Excess free energy can be minimized by the correct particle shape



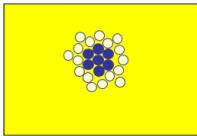
Since $dG=0$ when $r=r^* \rightarrow$ nuclei is in equilibrium with liquid:

Differentiation of $\Delta G_r = -\frac{4\pi}{3} r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}$ gives $r^* = \frac{2\gamma_{SL}}{\Delta G_v}$ and $\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_v)^2}$

Substituting ΔG_v : $r^* = \left(\frac{2\gamma_{SL}T_m}{L_v}\right) \frac{1}{\Delta T}$ and $\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2}\right) \frac{1}{(\Delta T)^2}$ - larger undercooling: smaller critical radius of the nuclei r^* .

Rate of homogeneous nucleation (see the slide below):

Homogeneous Nucleation



Instantaneous picture of the liquid → presence of many small close-packed clusters → temporarily exhibit the same crystalline array as the solid

Number of spherical clusters of radius r:

- liquid above T_m → all values r;
- liquid below T_m → only for $r \leq r^*$ → otherwise stable nuclei.

$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{k_B T}\right)$$

Excess free energy associated with cluster

Total number of atoms

Exercise 4.2: 1 mm³ of liquid copper (~10²³ atoms) at melting point contain about 10¹⁴ clusters of r=0.3 nm (~10 atoms) but only ~10 clusters with r=0.6 nm (~60 atoms). Maximum cluster size is ~100 atoms.
 - due to increasing contribution of ΔG_v with increasing undercooling → maximum cluster size increases with increasing ΔT

Energy approach: creation of nucleus as thermally activated process → solid-like cluster must be able to cross nucleation barrier ΔG^* and become nucleus → proportional to $\exp(-\Delta G^*/kT)$.

If liquid contains C_0 atoms per unit volume → number of critically sized cluster per unit volume

given by Arrhenius expression: $C^* = C_0 \exp\left(-\frac{\Delta G_{Hom}^*}{k_B T}\right)$

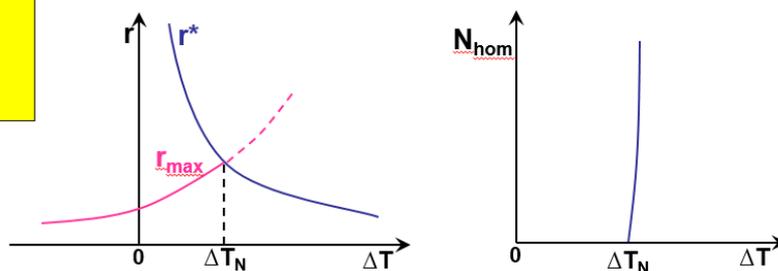
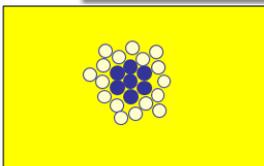
Frequency f_0 of addition of one more atom which make clusters nuclei:

$$\dot{N}_{Hom} = f_0 C_0 \exp\left(-\frac{\Delta G_{Hom}^*}{k_B T}\right) \text{ or } \dot{N}_{Hom} = f_0 C_0 \exp\left(-\frac{A}{(\Delta T)^2}\right) \text{ where } A = \frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2 k_B T}$$

- f_0 → complex function that depends on vibrational frequency, activation energy for diffusion in liquid and surface area of the critical nuclei;
- typical values for $C_0 \approx 10^{29}/m^3$; $f_0 \approx 10^{11}$;
- reasonable nucleation rate: 1/cm³s: ΔG^* has to be below 78kT!

Graphical relationship between the maximum cluster size and critical nuclei size and homogeneous rate of nucleation: (see slide below):

Homogeneous Nucleation



$$\dot{N}_{Hom} = f_0 C_0 \exp\left(-\frac{A}{(\Delta T)^2}\right)$$

- there is critical undercooling for nucleation ΔT_N ;
- experiments show that $\Delta T_N \approx 0.2 T_m$ for most of the metals
- in practice homogeneous nucleation is rarely encountered in solidification!!!
- ΔT_N is used to derive γ_{SL}

b) Describe unidirectional solidification in solid bar assuming that there is no diffusion in solid but there is perfect mixing in liquid. Sketch respective concentration profile of the solute along the solidifying bar as well as concentration profile in the liquid in front of the solidifying interface. Present and describe how variation of the solute concentration along the solidified bar can be estimated. Presentation of the relevant equations, sketch of the concentration profiles as well as motivation of the answer are necessary to get full credit. (3 p).

Answer:

Case 2: No Diffusion in Solid, Perfect Mixing in Liquid

- Liquid is kept homogeneous by efficient stirring;
- first solid will appear when T_1 is reached:

Since $kX_0 < X_0 \rightarrow$ solute is rejected in the liquid \rightarrow liquid become progressively richer in solute

Variation of the solute concentration along the solidified bar can be estimated using Scheil equations:

Case 2: No Diffusion in Solid, Perfect Mixing in Liquid

- mean composition of the solid \bar{X}_S is always lower than the composition at solid/liquid interface;
- variation of X_S along solidified bar \rightarrow equating solute rejected into the liquid when small amount of solid forms with the resulting solute increase in the liquid:

$$(X_L - X_S)df_s = (1 - f_s)dX_L$$

$f_s \rightarrow$ volume fraction solidified

Integrating using boundary conditions $X_S = kX_0$ when $f_s = 0$ gives:

$X_S = kX_0(1 - f_s)^{(k-1)}$

and

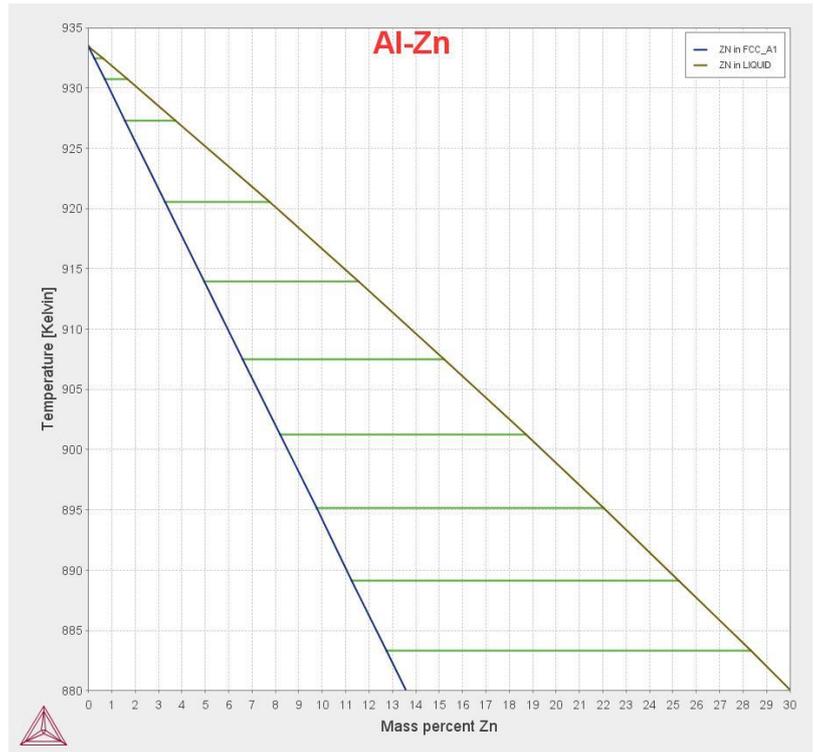
$X_L = X_0 f_L^{(k-1)}$

non equilibrium lever rule or Scheil equations

c) Using Al-Zn phase diagram, presented in the Figure, assuming that alloy is solidifying with no convection, evaluate for the composition Al-10 wt.%Zn:

- interface temperature at a steady state
- thickness of the diffusion layer
- temperature gradient required to maintain planar interface

The diffusion coefficient for the liquid $D_L=5 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ and speed of planar solid/liquid interface is $5 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$. (2p)



Answer:

- interface temperature at a steady state – solidus temperature for the composition concerned $\sim 893 \text{ K}$;

- Diffusion layer thickness: $D/v=10^{-3} \text{ m}$;

- Temperature gradient required to maintain planar interface: $\frac{dT_L}{dx} > \frac{T_1 - T_3}{D/v} = 24 \text{ K/mm}$

Where $T_1=917 \text{ K}$; $T_3=893 \text{ K}$ (from the phase diagram).

5. Diffusional transformations (7 p).

- Describe the reason for the nose-shape of the rate of homogeneous nucleation. Use homogeneous nucleation as an example. Presentation of the relevant equations, sketch of the $N=f(T)$ dependence as well as motivation of the answer are necessary to get full credit. (3 p).

Answer:

$$\dot{N}_{Hom} = fC_0 \exp\left(-\frac{\Delta G^*}{kT}\right)$$

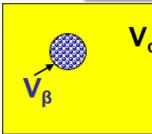
Nucleation rate during homogeneous nucleation contains frequency f of addition of one more atom which make clusters nuclei: $f = \omega \exp\left(-\frac{\Delta G_m}{kT}\right)$. f is proportional to the nucleus area and **diffusion** rate. Hence, it depends on the ΔG_m - activation energy for atomic migration per atom. ω is a factor describing atomic vibration frequency and area of critical nucleus. Therefore, nucleation rate during homogeneous nucleation depends in two parameters – barrier for

nucleation $\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v - \Delta G_s)^2}$ and activation energy for atomic migration ΔG_m :

$$\dot{N}_{Hom} = \omega C_0 \exp\left(-\frac{\Delta G_m}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right)$$

Following description in the slide below:

Homogeneous Nucleation



$\dot{N}_{Hom} = \alpha C_0 \exp\left(-\frac{\Delta G_m}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right)$

barrier for nucleation

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v - \Delta G_s)^2}$$

- ΔG_n - driving force for nucleation;
- $\Delta G_v - \Delta G_s$ - effective driving force for nucleation;
- ΔT_c - strain induced effective critical undercooling;

- $\Delta T < \Delta T_c \rightarrow N_{Hom}$ is negligible - G_v is too small;
- $\Delta T > \Delta T_c \rightarrow N_{Hom}$ is negligible - diffusion is too slow;
- N_{Hom} is maximal at $\Delta T \approx \Delta T_c$;

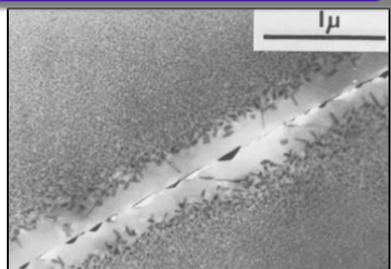
- $\Sigma\gamma A \rightarrow \min$; so $\Delta G^* \rightarrow \min$: smaller ΔT_c ;
- If small ΔG_s (low misfit) and small γ (coherence) \rightarrow homogeneous nucleation is possible

b) Describe the difference in the initial rate of the GP zone formation depending on the temperature, from which alloy is quenched before age-hardening. Describe the reasons for the presence of the precipitate-free zone (PFZ) in case of the age-hardening alloys and how it can be avoided/minimized. (2p)

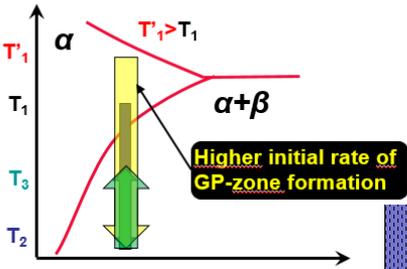
Answer: Slide below.

Quenched-in Vacancies

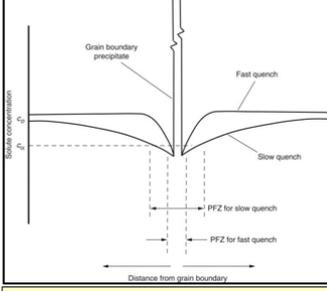
- high temperature \rightarrow high vacancy concentration;
- quenching \rightarrow vacancies trapped in vacancy cluster \rightarrow nucleation sites for GP-zones;
- enhancing diffusion rates at aging temperatures;
- higher concentrations after higher solution treatment temperatures:



Precipitate-free zone in an Al-Zn-Mg alloy



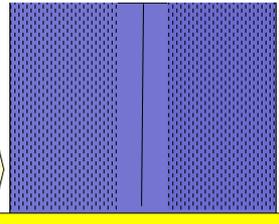
Higher initial rate of GP-zone formation



Precipitate-free zone (PFZ) width as function of quench rate

Precipitate-free zone (PFZ):

- absence of precipitation close to grain boundaries. Reasons:
- vacancies "sinks" in grain boundaries;
- grain boundary precipitation.



depleted grain boundary zone

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

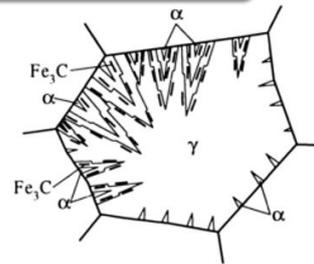
c) Describe the differences between the upper and lower bainite: nucleation, structure, orientation relationship to the primary austenitic grain, carbide morphology and precipitation, temperatures of formation. Motivation of the answer are necessary to get full credit. (2p)

Answer: slides below

Bainite transformation

Upper bainite (350-550°C)

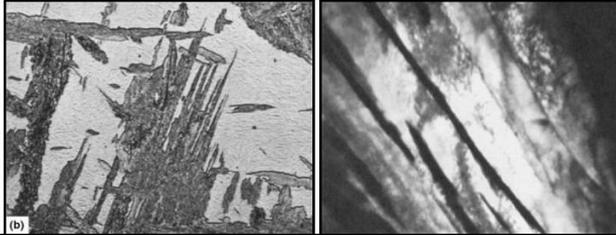
- needles or laths of ferrite;
- cementite precipitates between laths;
- nucleates on grain boundary, similar to Widmanstätten side-plates;
- large undercooling → low energy semicoherent interfaces;
- orientation relationship to γ -grain for ferrite and cementite (not the case for pearlite);
- discontinuous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



Schematic of mechanism in the formation of upper bainite.

Upper bainite in 4360 steel - carbide particles (dark) formed between ferrite crystals

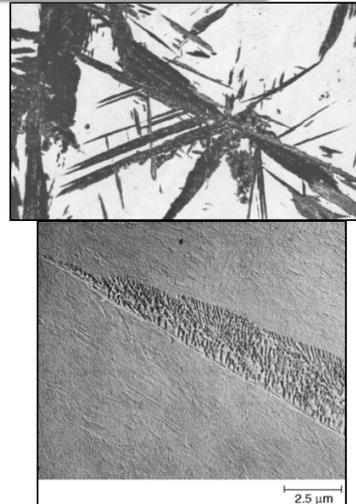
Volume 3, Alloy Phase Diagrams → Nonequilibrium Reactions—Martensitic and Bainitic Structures → Bainitic Structures



Bainite transformation

Lower bainite – formed at ~ 350°C;

- plates of ferrite;
- cementite or transition carbides (e.g. ϵ -carbide) precipitate in and to lower extent between plates;
- transition temperature depends on carbon content:
 - i) increases with C-content for $C < 0.5 \text{ wt. \% C}$;
 - ii) decreases when $0.5 \text{ wt. \% C} < C < 0.7 \text{ wt. \% C}$;
 - iii) constant for $C > 0.7 \text{ wt. \% C}$ - around 350°C;
- large undercooling: low energy semicoherent interfaces;
- orientation relationship to γ and between ferrite/cementite;
- the same habit plane for ferrite as for martensite that can be formed in the same alloy;
- different transformation kinetics → sometimes separate C-curves on TTT diagram.



Lower bainite formed at 345°C in 4360 steel.

ASM handbook-Volume 9, Metallography and Microstructures → Bainitic Structures → Lower Bainite

6. Diffusionless transformation (4 p)

- a) Describe formation and crystallography of martensite – namely, structure, Bain model and the ways how the strain of the surrounded austenite can be compensated. Motivate your answer to get full credit. (3p)

Answer:

- microstructure → within a given grain all the plates grow in a limited number of orientations;
- orientation and plate morphology strongly depend on alloy composition → especially carbon and nickel;
- problem: high speed of growth requires high mobility of interface moving on γ -planes → but not always dislocation glide plane → how does this work?
- habit plane is observed to be undistorted macroscopically;
- for habit plane to be undistorted during growth:
 - homogenous shear parallel to habit plane;

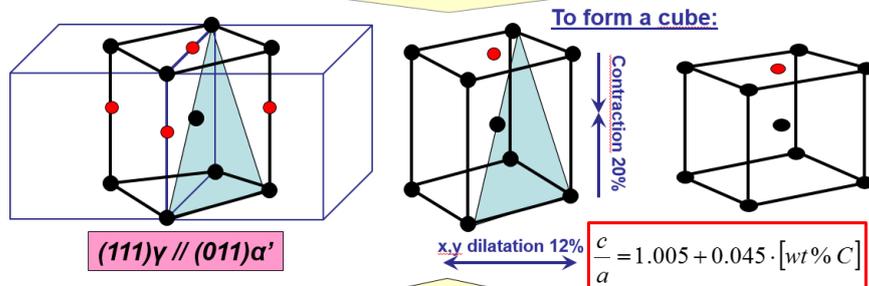
- 4% expansion normal to habit plane.

Bain model:

The Bain Model of the fcc → bcc Transformation

Bain model → **bcc** lattice can be obtained from **fcc** with the minimum atomic movement and surface strain:

- elongated **bcc** lattice can be drawn within two **fcc** cells;
- transformation to **bcc** cell by contracting cell 20% in **z**-direction and expanding 12% in **x** and **y** axes:

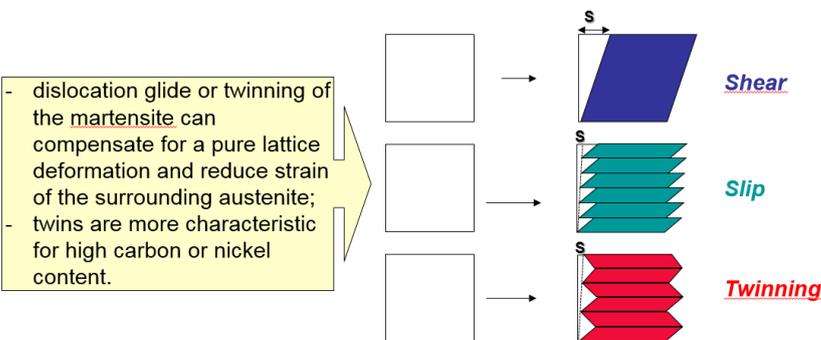


- orientational relationship - Kurdjumov-Sachs or Nishiyama-Wasserman:
 - $\{111\}_\gamma // \{011\}_{\alpha'}$;
- Bain deformation involves the absolute minimum of atomic movement in generating **bcc** from **fcc** lattice;

In order to fulfil the requirements of transformation with an undistorted plane, additional distortion has to be postulated:

The Bain Model of the fcc → bcc Transformation

- Bain deformation alone does not fulfil the requirements of transformation with an undistorted plane;
- additional distortion has to be postulated → dislocation slip or twinning:
 - alternate regions in austenite undergo Bain strain along different contraction axes → net distortions are compensated;
 - habit plane of the plate can adopt any desired orientation by adjusting the width of individual twins.



- b) Describe the role of dislocation in martensite nucleation. Presentation of the relevant equations as well as motivation of the answer are necessary to get full credit. (1p)

Answer: slide below

Role of Dislocations in Martensite Nucleation

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: $\gamma \rightarrow \epsilon' \rightarrow \alpha'$:
 - no evidence of $\epsilon' \rightarrow \alpha'$ transformation;
 - ϵ' and α' form independently.

Disslocation strain energy assisted deformation:

- strain field associated with dislocation provide favorable interaction with the strain field of nucleus:

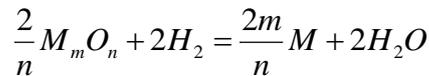
$$\Delta G = -V\Delta G_v + A\gamma + V\Delta G_{Strain} - \Delta G_{dislocation}$$

Disslocation interaction energy → reduces the nucleation energy barrier! $\Delta G_d = 2\mu s \pi a c b$

- 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.

7. Solid/gas interactions (2 p)

During sintering of the admixed powder metallurgy steels, containing iron powder (base), nickel and chromium powder (alloying elements), full reduction of the surface oxides, covering powder particles, is required to provide good inter-particle bonding and diffusion of the alloying elements. Estimate maximum tolerable pressure of the water vapour in the system during sintering in the $N_2/10\%H_2$ atmosphere at 1100 °C to provide efficient reduction of the all surface oxides, presented



in the system. Equation of the reducing reaction:

$\Delta G(NiO) = -110.877$ kJ; $\Delta G(FeO) = 6.530$ kJ; $\Delta G(Cr_2O_3) = 178.983$ kJ

Answer:

Equations: $\frac{2}{n} M_m O_n + 2H_2 = \frac{2m}{n} M + 2H_2O$ $K = \frac{p^2(H_2O)}{p^2(H_2)}$ $\frac{p(H_2)}{p(H_2O)} = \exp \frac{\Delta G_2^0}{2RT}$

$$p(H_2O) = \frac{p(H_2)}{\exp \frac{\Delta G_2^0}{2RT}}$$

Powder particles are covered by respective oxides (iron particles by FeO, nickel particles by NiO and so on). Calculate based on the partial pressure of hydrogen (0.1 bar) and requirements for the most stable oxide (Cr_2O_3) – can be seen from Gibbs free energy or lower partial pressure of the water vapor obtained for oxides of interest. In this case - maximum tolerable water vapour pressure in the system at $T = 1100^\circ C$ required to provide reduction of mentioned above oxides - most stable oxide (Cr_2O_3) - is $p(H_2O)_{Cr_2O_3} = 3.94e-5$ bar.