MSE-422 - Advanced Metallurgy

Exam 24/01/2024

09h15 – 10h45

Family name:____

First name:____

No. Sciper:____

Question	**Points**
1	/15
2	/17
3	/13
4	/15
5	/15
Total:	**/75**
Grade:	

- Do not write more text than is necessary; sometimes, you can answer the questions with 1-2 words.
- You can also write on the backside of the sheets. If you do so, please indicate clearly to which question your answer belongs.
- If you need more paper for your answers, please ask.

1) Advanced steels (15P)

a) In Table 1, the chemical compositions of several steels are listed in wt.%. Their SEM images are respectively shown in Figure 1.

- Please complete the table by adding their EN steel name designation. (2P)

Table 1: Designations and compositions of four different steels;

Nr	Steel	C	Cr	Ni	Mn	Si	Mo	Al
1	X61Mn24	0.61			24			
2	X10MnSiAl6	0.10			6	0.3		0.6
3	17MnSiAl6	0.17			1.5	0.15		0.03
4	13MnSiCrNiMoAl6-1	0.13	0.04	0.05	1.5	0.25	0.02	0.04

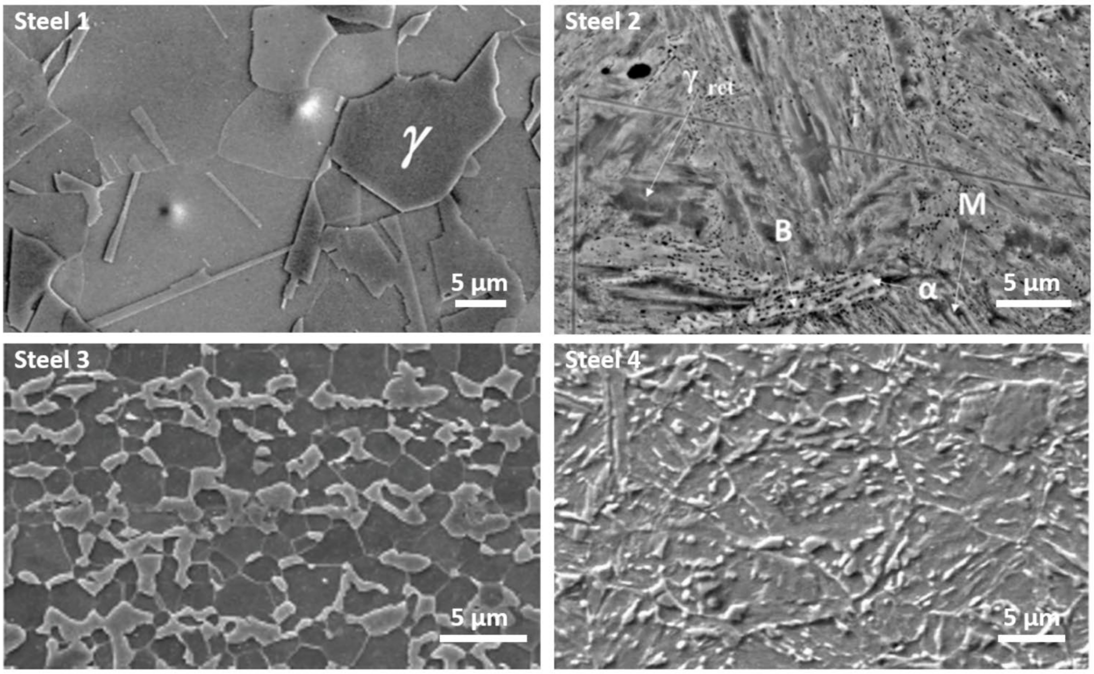

Figure 1. SEM images of steels 1-4;

- Associate the steel numbers in Table 1/Figure 1 to the following types of steels and justify your answer briefly: DP, CP, TRIP, and TWIP steels. (2P)
  Steel 1: TWIP; primary austenite phase; high Mn content;
  Steel 2: TRIP; retained austenite, ferrite, and bainite phases;
  Steel 3: DP; ferrite and martensite phases;
  Steel 4: CP; ferrite, bainite, and martensite;

- The above-mentioned steels have different mechanical properties. Fill in the missing labels in Figure 2 using DP, CP, TRIP, and TWIP. (2P)

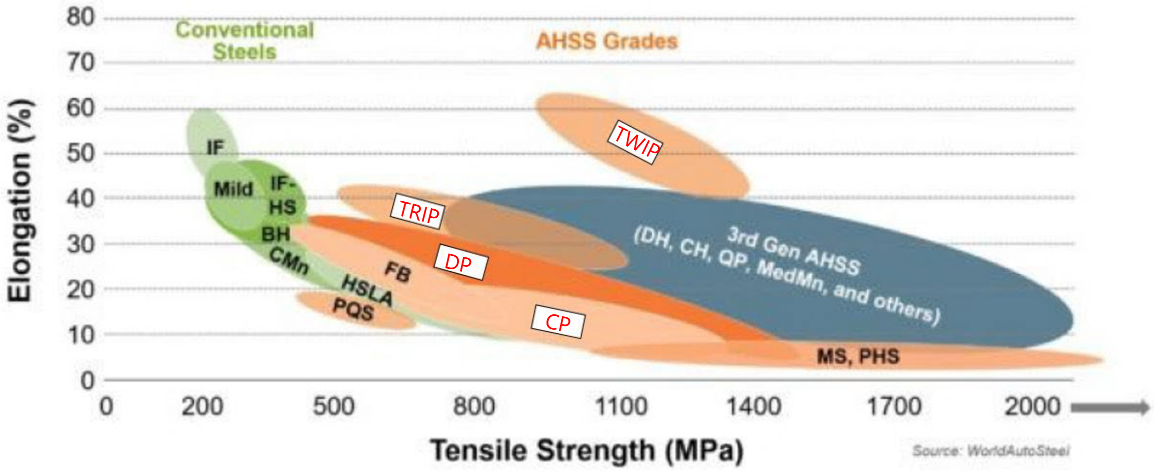

Figure 2. Comparison of mechanical properties of different steels;

b) Figure 3 demonstrates two heat treatment routes to obtain a DP steel (the volume fractions of the two phases are 70% and 30%).

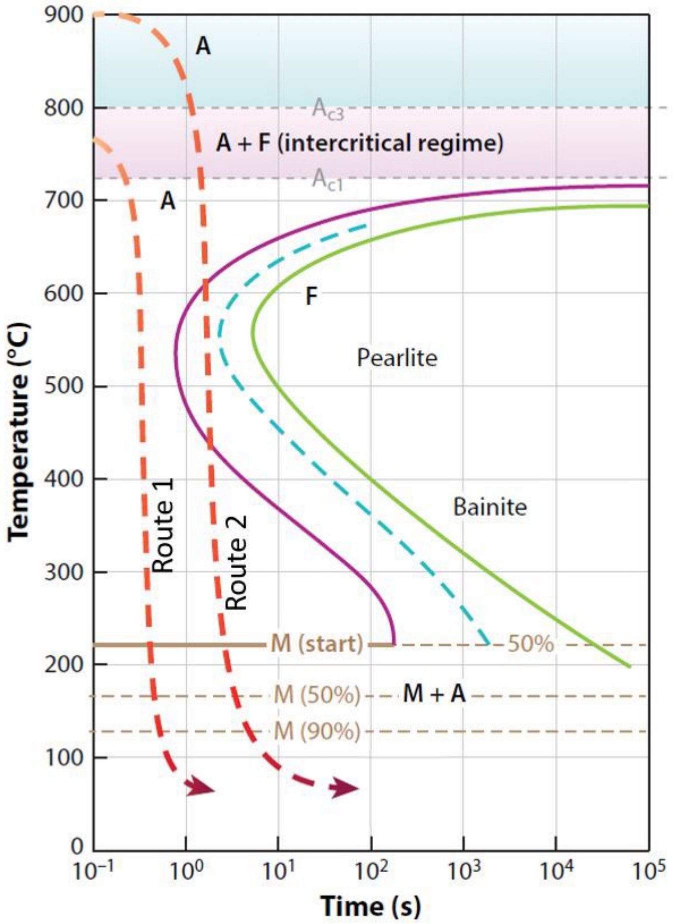

Figure 3. TTT diagram indicating the heat treatment methods of a DP steel;

Describe the two routes then identify the initial and the final phases with their respective volume fractions. (2P)

Route 1: Annealing in an intercritical (austenite-ferrite) regime, then rapidly quenching and holding at a temperature below the martensite start temperature.

Initial phases are 70% ferrite and 30 % austenite. Final phases are 70% ferrite and 30 % martensite.

Route 2: Annealing in a fully austenite regime, then quenching (with an adjusted rate) and holding at a temperature below the martensite start temperature. The quenching rate is adjusted so that most of the undercooled austenite transforms to ferrite.

Initial phase is 100 % austenite. Final phases are 70% ferrite and 30 % martensite.

- Briefly explain the physical meaning of temperatures A_{c1} and A_{c3}. (1P)

  A_{c1}: the temperature at which austenite begins to form during heating

  A_{c3}: the temperature at which the transformation from ferrite to austenite is completed during heating

- How do the different phases in DP steels contribute to the mechanical properties? (1P)

  DP steels have a microstructure of ferrite with martensite islands. The soft ferrite matrix provides good ductility, while the hard martensite islands contribute to high strength and toughness.

c) Quenched and Partitioned (Q&P) steels belong to the 3rd generation AHSS. In general, Q&P steels have a composition of 1-1.5 wt.% Mn, 0.1-0.3 wt.% C, and 0-1.5 wt.% Al. Figure 4 demonstrates the heat treatment of a Q&P steel.

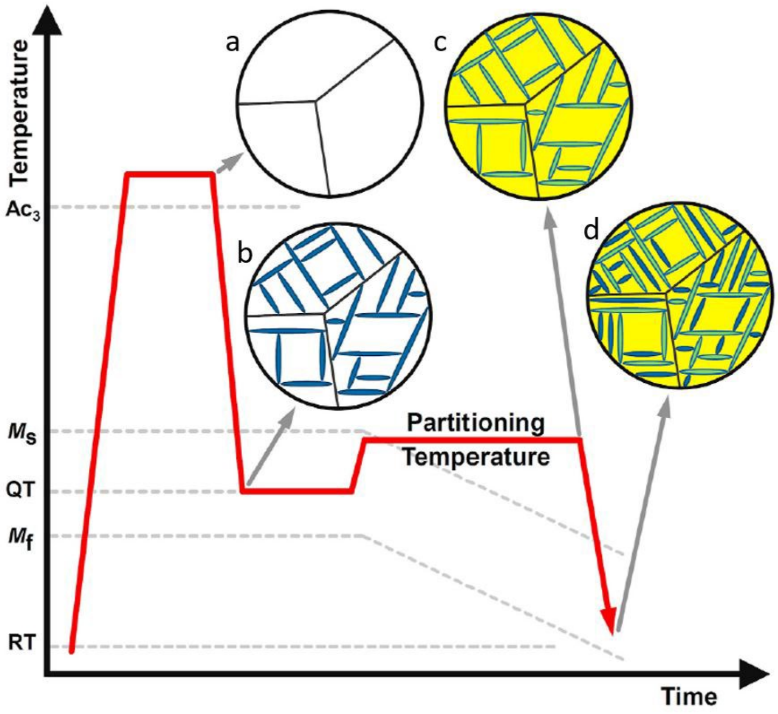

Figure 4. Schematic of the heat treatment process of a Q&P steel;

- What are the phases shown in the microstructures of a-d in Figure 4? Explain briefly what happened during the "partitioning" process. Why did the temperatures M_s and M_f decrease during partitioning? (3P)
  a: austenite; b: austenite and martensite; c: carbon-enriched austenite and carbon-decreased martensite; d: carbon-enriched austenite, carbon-decreased martensite, and martensite.
  During partitioning, carbon transports from martensite to austenite.
  M_s and M_f decrease because the increase of carbon content in austenite can stabilize the austenite phase and lower the martensite formation temperature.

- The volume fraction of the retained austenite at stage "d" in the above Q&P steel was observed to first increase and then decrease with increasing quench temperature (QT in Figure 4). Provide a possible explanation for this phenomenon. (2P)
  When the QT starts to increase from M_f, the volume fraction of untransformed austenite increases. However, if the QT is too high, the partitioning process cannot effectively pump carbon into the austenite phase because of its high volume fraction, resulting in low stability of the untransformed austenite (the decreases in M_s and M_f are less pronounced). Therefore, more austenite transforms to martensite during the final quenching, i.e., less retained austenite.

2) Nickel and Titanium alloys (17P)

You recently joined an Aerospace company as a material expert and you are responsible for the selection, processing and characterization of high-performance Ni and Ti alloys

a) Your team leader gave you the following scanning electron micrograph (Figure 5), which shows the cross section of a single crystalline turbine blade of the alloy CMSX-4 after 1'000 h of service with a maximum temperature of 950°C in an aero-engine. The alloy has the composition (in wt.%) given in Table 2.

Table 2: Chemical composition of CMSX-4;

Ni	Cr	Co	Mo	Al	Ti	Ta	Hf	Re
Bal.	6.5	9	0.6	5.6	1.0	6.5	0.1	3.0

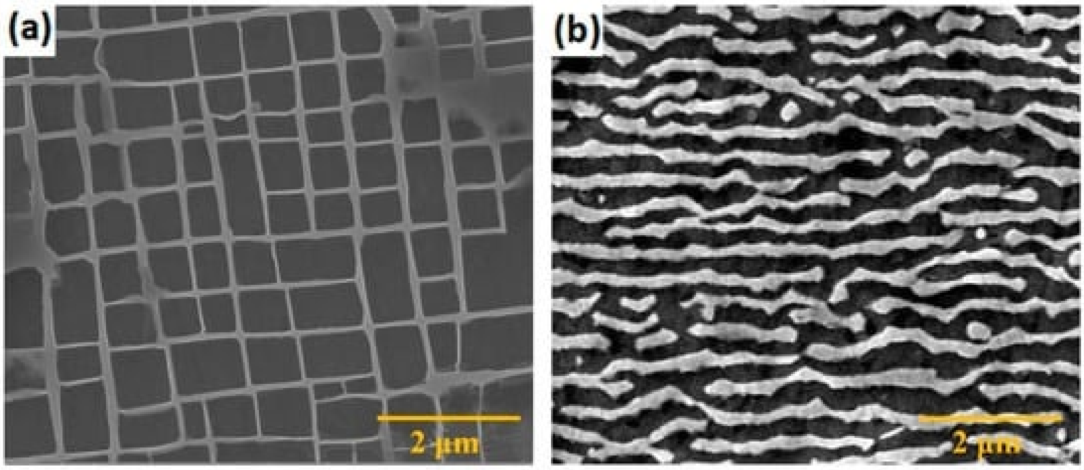

Figure 5. SEM – Cross section of a single-crystal turbine blade before and after 1'000 h of operation

- Name the phases that can be seen in the micrograph (1P)

  γ/γ’

- Explain the role of the alloying elements Cr and Re. (2P)

  Cr: forms Cr-rich protective layer, solid solution strengthener (carbide former, less so in CSMX-4)

  Re: solid solution strengthener, delay coarsening of γ’ (reduction of γ/γ’ lattice mis-fit)

- Explain the microstructural changes that can be observed between the two micrographs. What is the common name for this phenomenon? (3P)

  Rafting;

  - Directional coarsening is caused by the superposition of external load stresses and internal coherence stresses
  - If the γ'/γ lattice mismatch is positive ($a\gamma < a\gamma'$) ⍰ type P
  - If the γ'/γ lattice mismatch is negative ($a\gamma > a\gamma'$) ⍰ type N (most frequent case)
  - This results in different local stress fields in the γ channels perpendicular and parallel to the loading direction

  These stress differences are the driving force for a directional diffusion; the γ' particles grow in the direction of the lower lattice distortion in the γ channels

b) Your team leader shares the results from stress rupture tests performed at different test parameters on Ni-based super alloy used for turbine blades (shown in Figure 6). Consider that $LMP = T(\ln(t) + c) \times 10^{-3}$ and that the Larson miller parameter constant c is 25.

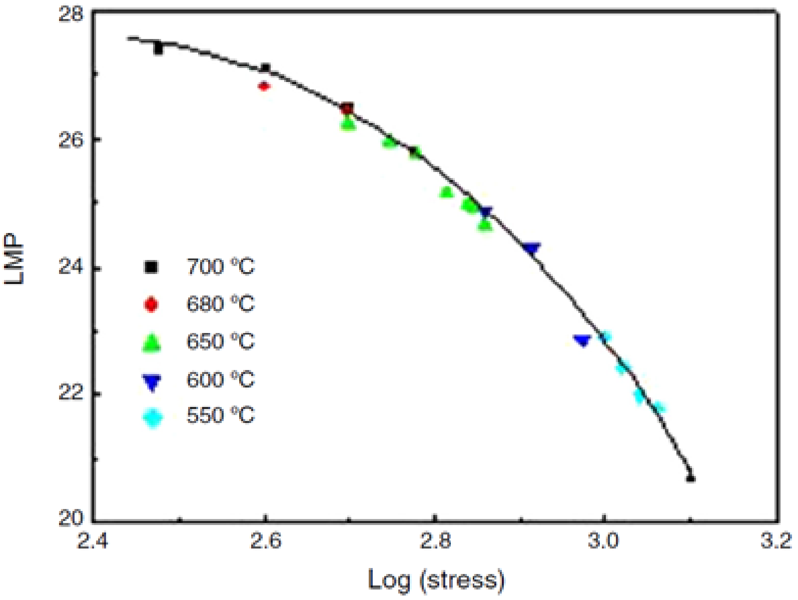

Figure 6. Larson Miller Parameter (LMP) correlation with stress obtained from stress rupture test of Ni-based super alloy.

- What stress can be applied so that the service life of the alloy at 500°C is 6000 h. (3P)

  $LMP = 773 (\ln(6000) + 25)$

  $= 26049$

  $= 26000$

  $\log \sigma = 2.75$

  $\sigma = 562$ MPa

- Additionally, your team leader wishes to have a safety factor of 10% considering the testing uncertainty. What will be your suggested stress for application of the alloy at 500°C is 6000 h? (1P)

  Considering the safety factor = 562 x 0.9 = 506 MPa

c) You are supposed to investigate the microstructure of a landing gear part of an airplane, which has been fabricated by Laser Powder Bed Fusion (LPBF) from the titanium alloy Ti-6Al-4V. LPBF is an additive manufacturing (or 3D-printing) process, in which a fine powder of the alloy is deposited layer by layer and then melted with a fast scanning high power laser (500W) to form parts with complex geometries. The laser spot diameter is typically around 100 µm and the laser scan velocities are on the order of 500-1000 m/s.

- What category of Ti alloys does Ti-6Al-4V belong to? (1P)

  It belongs to α+β titanium alloys.

- Explain the role of V and Al. (1P)

  V acts as β phase stabilizer, and Al acts as α phase stabilizer.

- The EBSD map given in Figure 7 illustrates the microstructure of the part after the LPBF process. What is the name of the phase that has formed? Explain why this phase is pronounced after Laser Powder Bed Fusion. (2P)

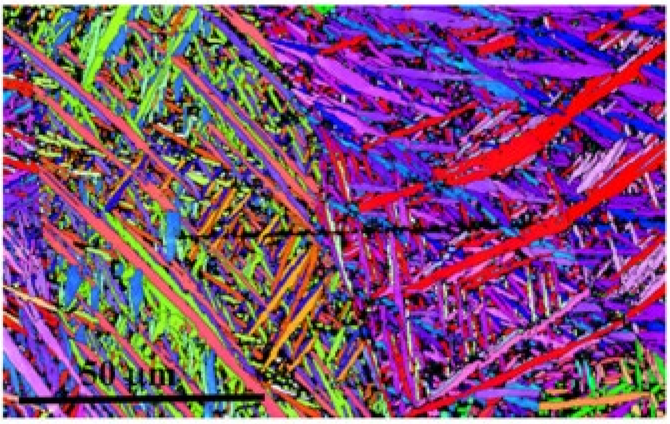

Figure 7. EBSD map of a Ti6Al4V alloy built after Laser Powder Bed Fusion

The needle grains belong to α martensite phase, which is formed during LPBF because of the high cooling rates.

d) You heat treat the sample from question c at 1000 °C and then you cool it down to room temperature with

   i. furnace cooling and
   ii. quenching into water.

What changes in the phases of the microstructure do you expect? How will these changes affect the ductility and the ultimate tensile strength of the alloy qualitatively? (3P)

The heat treatment is conducted at the β-field. Furnace cooling will result in the dispersion of β phase within the matrix of α phase, while water quenching will propote the formation of α martensite. The duplex α+β microstructure has a better trade-off between ductility and UTS, while the α martensite microstructure has higher UTS but lower ductility.

3) Aluminium alloys (13P)

a) Consider two alloys with the following designation: AA6061-T6 and AA514.0. Based on this information, please name:

- The category of alloys these materials belong to. (1P)
  AA6061—Wrought aluminium alloy and AA514.0: cast Al alloy

- Their main alloying elements and the impact of these elements. (2P)
  AA6061-Mg and Si (solid solution and precipitation strengthening) and AA514.0: Mg

- What does the designation T6 stand for? (1P)
  T6: peak aging (optimum condition for maximum hardness)

b) The figure below shows the binary Al-Ge phase diagram. Complete the phase diagram by adding the missing phases in each phase field. (2P)

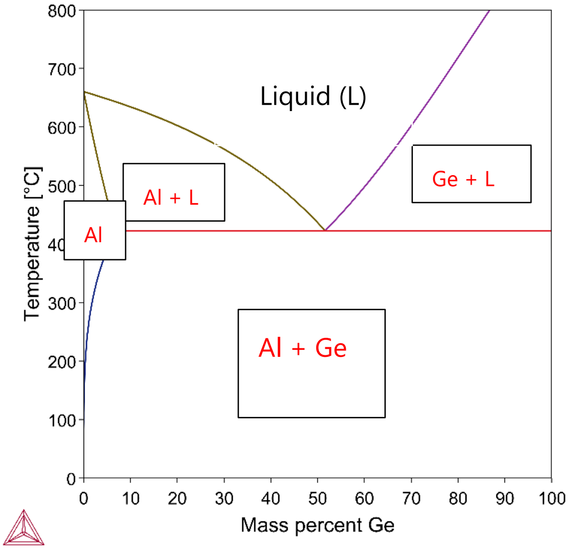

Figure 8. binary Al-Ge phase diagram

c) The figure below shows the EBSD grain orientation maps of an AA3003 alloy in the as-cast condition and one after hot rolling. Indicate which EBSD map (a or b) is attributed to the as-cast condition and which one to the hot-rolling and justify your answer. (1P)

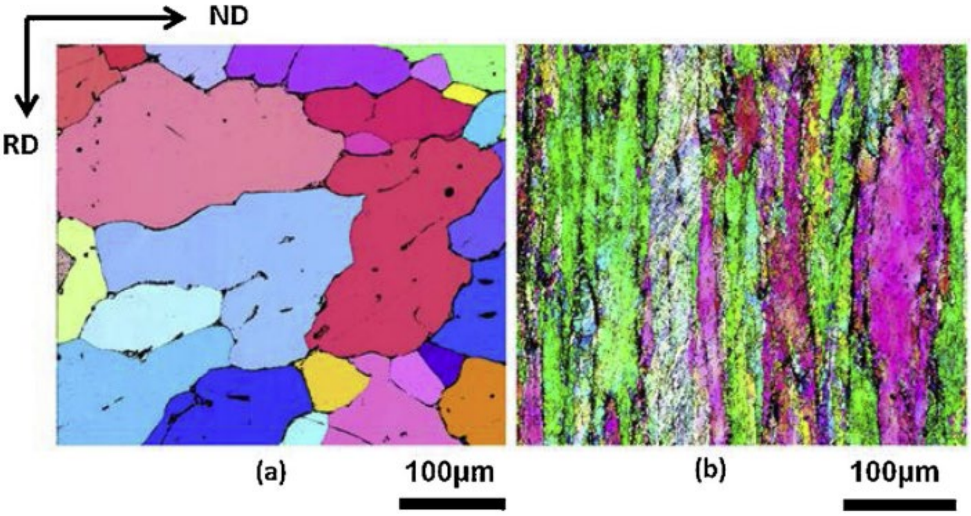

Figure 9. EBSD grain orientation maps of an AA3003

EBSD a: cast (larger grains randomly distributed), b: rolled (grain orientation)

d) You have been given the heat treatment protocol for the alloy AA2017. Consider that two main phases are appearing in this alloy in the solid state (Al-FCC and Al_2Cu):

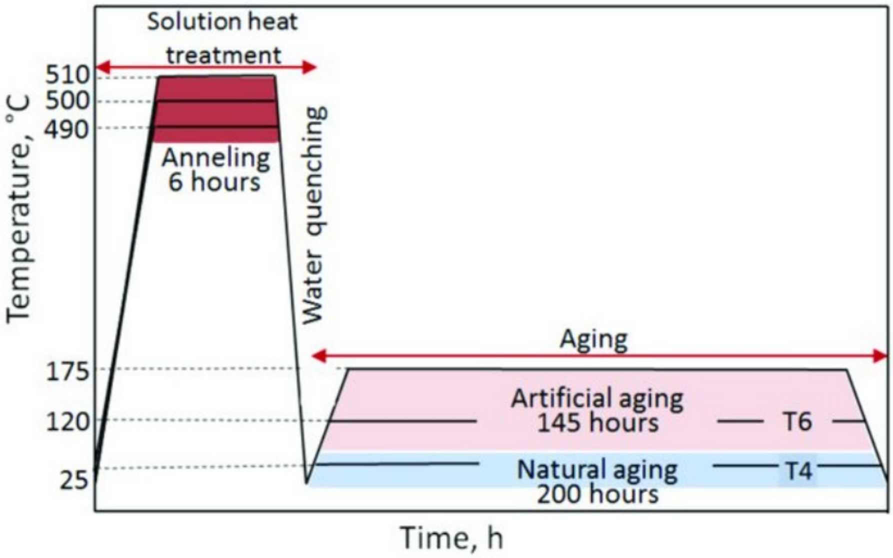

Figure 10. Heat treatment (T-t-profle) for AA2017

- Which phases appear in the microstructure after the solution treatment and which after the aging step. Justify your answer. (2P)
  Al_FCC after solution treatment and Al_FCC + Al_2Cu after ageing

- Explain which strengthening mechanism is more important after the solution treatment step and which after the aging step. (2P)
  Solution strengthening after solution treatment and precipitation hardening after the ageing treatment

- What impact would the increase of the temperature of artificial aging have on the hardness of the material, the number density and the size of the precipitates? Justify your answer. (2P)
  Drop of hardness, drop of number density, increase of the size of the precipitates

4) High Entropy Alloys and Bulk Metallic Glasses (15P)

a) Calculate the entropy of mixing (S_{mix}) for an equimolar five-component HEA, FeCoNiCrCu, knowing that the ideal gas constant is 8.3 J·K^{-1}·mol^{-1}. (1P)

$S_{\mathrm{mix}} = R\ln N = 8.3 \times \ln 5 = 13.36$ J·K^{-1}·mol^{-1}

b) Calculate the enthalpy of mixing (H_{mix}) for the above-mentioned HEA, assuming a constant interaction parameter Ω = 8 kJ ·mol^{-1}. (1P)

$H_{\mathrm{mix}} = \frac{1}{2}\Omega\left(1 - \frac{1}{N}\right) = \frac{1}{2} \times 8 \times \left(1 - \frac{1}{5}\right) = 3.2$ kJ ·mol^{-1}

c) In reality, a HEA cannot achieve the ideal mixture. Therefore, a correction term, the excessive entropy (S_E), as a function of atomic packing and atom size is introduced for the entropy of mixing. S_E is negative and $|S_E|$ is positively related to the size mismatch of the atomic radii (δ). In fact, the entropy of mixing calculated in question a) represents the configurational entropy of mixing (S_C). In practice, the entropy of mixing is expressed as: $S_{\mathrm{mix}} = S_C + S_E$.

A dimensionless thermodynamic parameter has been proposed for the design of HEAs:

$$\phi = \frac{S_C - \frac{H_{\mathrm{mix}}}{T_m}}{|S_E|}$$

Knowing that the average melting point, T_m, of the five components in HEA FeCoNiCrCu is 1450 °C and $|S_E|$ is 0.031 J·K^{-1}·mol^{-1}, calculate the ϕ parameter for this HEA. (1P)

$$\phi = \frac{S_C - \frac{H_{mix}}{T_m}}{|S_E|} = \frac{13.36 - \frac{3.2 \times 1000}{1450 + 273.15}}{0.031} = 371$$

d) Al has been added to the equimolar HEA FeCoNiCrCu. With increasing content of Al, the valence electron concentration (VEC) is reduced. The VEC values of Fe, Co, Ni, Cr, Cu, and Al are 8, 9, 10, 6, 11, and 3, respectively. Assuming the second phase starts to form in this FeCoNiCrCu + Al system when its VEC = 8.1, calculate the molar fraction of Al at this critical point. What are the lattice structures of the primary phase and the second phase? (2P)

Average VEC of FeCoNiCrCu: $\mathrm{VEC_{avg}} = \frac{8+9+10+6+11}{5} = 8.8$

Average VEC of FeCoNiCrCu + Al: $8.1 = 8.8(1 - x_{\mathrm{Al}}) + 3x_{\mathrm{Al}}$

Therefore: $x_{\mathrm{Al}} = 0.12$

The primary phase is FCC and the second phase is BCC.

e) Calculate the configurational entropy of mixing (S_C) and the enthalpy of mixing (H_{mix}) for the FeCoNiCrCu + Al system with critical Al content mentioned in d), assuming a constant interaction parameter Ω_{Al} = -50 kJ ·mol^{-1} between Al and other elements and a constant interaction parameter Ω = 8 kJ ·mol^{-1} between Fe, Co, Ni, Cr, and Cu. (2P)

$S_C = -R\sum x_i \ln x_i = -8.3 \times (5 \times 0.176 \times \ln 0.176 + 0.12 \times \ln 0.12) = 14.8$ J·K^{-1}·mol^{-1}

$H_{\mathrm{mix}} = \sum_{i=1}^{N-1}\sum_{j>i}^{N} x_i x_j \Omega_{ij} = 10 \times 0.176^2 \times 8 + 5 \times 0.176 \times 0.12 \times (-50) = -2.8$ kJ·mol^{-1}

f) Knowing that the melting point of Al is 660 °C and the excessive entropy (S_E) of this critical system is 0.83 J·K^{-1}·mol^{-1}, calculate its ϕ parameter. According to previous research, this ϕ value is very close to the critical value to distinguish single-phase HEA and multiphase HEA. Do you expect higher or lower |ϕ| values for BMGs compared to HEA FeCoNiCrCu? Justify your answer briefly. (2P)

Average melting point: $T_m = (1450 + 273.15) \times 0.88 + (660 + 273.15) \times 0.12 = 1628\ \mathrm{K}$

$$\phi = \frac{S_C - \frac{H_{mix}}{T_m}}{|S_E|} = \frac{14.8 - \frac{-2.8 \times 1000}{1628}}{0.83} = 20$$

Lower |ϕ| values for BMGs.

Reason: higher $|S_E|$ because of significant difference in atomic sizes.

g) Explain the "confusion principle" for bulk metallic glasses (BMG) along with the Turnbull criterion (2P).

At least three elements capable of producing different crystalline structures

A significant difference in atomic sizes of the main 3 constituents of the system (more than 12%)

The heat of mixing of each pair of the main three elements should be quite negative

According to Turnbull, the position of the glass transition temperature Tg relative to the melting point Tm is relevant for the glass forming ability. The reduced glass transition temperature Trg is defined as

T_rg=T_g/T_m

Explain two different fabrication routes for BMGs with a schematic. (2P)

Melt spinning, splat quenching, suction Cu mold casting, laser-based additive manufacturing

h) Explain the plastic deformation mechanism of BMGs (2P).

Since there are no dislocations, plastic deformation in metallic glasses is accommodated by localized irreversible rearrangement of atomic regions, involving tens of atoms, i.e. so-called Shear Transformation Zones (STZs) The shear transformation zones require some free volume accumulation and shear band formation forms additional free volume

5) Process Metallurgy (15P)

Steel and aluminium are key materials in the global economy and modern civilization, serving as the backbone of infrastructure, energy, industry, manufacturing, safety, and transportation systems. More than 1'900 Mt of steel and 100 Mt of aluminum are currently produced per year. Both metals are obtained from their metal ores, mainly hematite (Fe_2O_3) and Bauxite (Al_2O_3).

NOTE: you may use the Ellingham diagram on the last page for answering the questions below

a) The most relevant process for steelmaking is the blast furnace + oxygen converter process. In the blast furnace, hematite is reduced according to the following net reaction:

$$Fe_2O_3 + 6CO = 2Fe + 3CO_2 + 3CO$$

Coke containing 96.5% C is used to produce CO by combustion with air at the bottom of the furnace. Of the coke charged, 92.5% are burnt to CO.
M[Fe] = 55.85 g/mol; M[C] = 12.01 g/mol; M[O] = 16.00 g/mol; V_m(gas) = 22.41 l/mol

- Calculate the mass of coke required to produce one batch of 5t of crude iron (3P)

  Moles of Fe: $\frac{m_{Fe}}{[Fe]} = \frac{5000\text{ kg}}{0.055845\text{ kg/mol}} = 89'526\text{ mol}$

  2 mol Fe ~6 mol CO --> Moles of CO: $268'578$ mol

  1 mol C = 1 mol CO --> 268'578 mol C ~ 3'225'622 g C m = 3'225.622 kg C

  Required mass of C (total) = $\frac{3225622}{0.925} = 3'487'159\ g$

  Required mass of Coke (total) $= \frac{3487159}{0.96} = 3'709'743\ g = 3.61\ t\ coke$

- Calculate the mass of the CO_2 resulting from the production of 5t of crude iron (1P)

  2 mol Fe ~3 mol CO2 --> factor 1.5

  89'526 mol Fe ~ 134'289 mol CO2

  With M[CO2] = 44.01 g/mol -->m[CO2] = 134'289 mol * 44 g/mol = 5'910'059 g17

b) What is the role of lime (CaO) and/or lime stone ($CaCO_3$) in the blast furnace process? (1P)
CaO and CaCO3 are slag formers --> reacts with silicate and phosphorous impurities from the molten iron

c) In the recent years, the HYBRIT direct reduction process, in which hydrogen is used as the reducing agent, has been developed by the Swedish steel manufacturer SSAB

- Re-write the chemical reaction above assuming that pure hydrogen gas is used for the reduction of hematite. (1P)

  $Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$

- Name two advantages of the HYBRIT process in comparison with the conventional blast furnace process (2P)

  - No CO_2 is produced, just water
  - The direct reduction process is comparatively energy efficient. Steel made using DRI requires significantly less fuel, in that a traditional blast furnace is not needed

d) The most relevant process for aluminium-making is the Hall-Héroult process, in which Bauxite is converted into pure Al in an electrochemical process.

- Explain why Al_2O_3 is mixed with cryolite Na_3AlF_6 in the process. (1P)

  Al_2O_3 is mixed with cryolite Na_3AlF_6 to form a eutectic with a comparably low melting point --> less heat/energy required for heating

- Explain the difficulties with the direct reduction of Al_2O_3 (i.e. not in an electrochemical process) that would occur if Coke would be used as the reacting agent, similar to the steelmaking process, according to the reaction $Al_2O_3 + 3C = 2Al + 3CO$ (2P)

  According to Ellingham diagram, C reacts with Al_2O_3 only at $T>2000$°C
  --> challenging to realize in industrial furnaces

- Explain why the use of recycled Al scrap is a good solution for fast decarburization of this sector. (2P)

  - Aluminium can be easily recycled
  -melting of Al consumes much less energy due to the low melting point of Al
  - Challenge: The high reactivity of Al and the stability of Al-based IMCs lead to the presence of e.g. Cu or Fe within the different types of Al alloys which is a major limitation to achieve high quality secondary Al

- Aluminothermic welding, in which Al powder is mixed with hematite (Fe_2O_3) and ignited with a heat source, is used for e.g. welding of railway tracks without using electric power supplies. Briefly explain with a chemical reaction and the use of the Ellingham diagram what is happening in this process and why. (2P)

  2Al + Fe2O3 --> 2Fe + Al2O3

  Al2O3 is the more stable oxide, so Al will 'steal' the oxygen from the Fe. The reaction is highly exothermic, resulting in temperatures of up to 2'400°C. Iron melts and flows between the tracks (welding) while Al2O3 floats on top of the liquid Fe

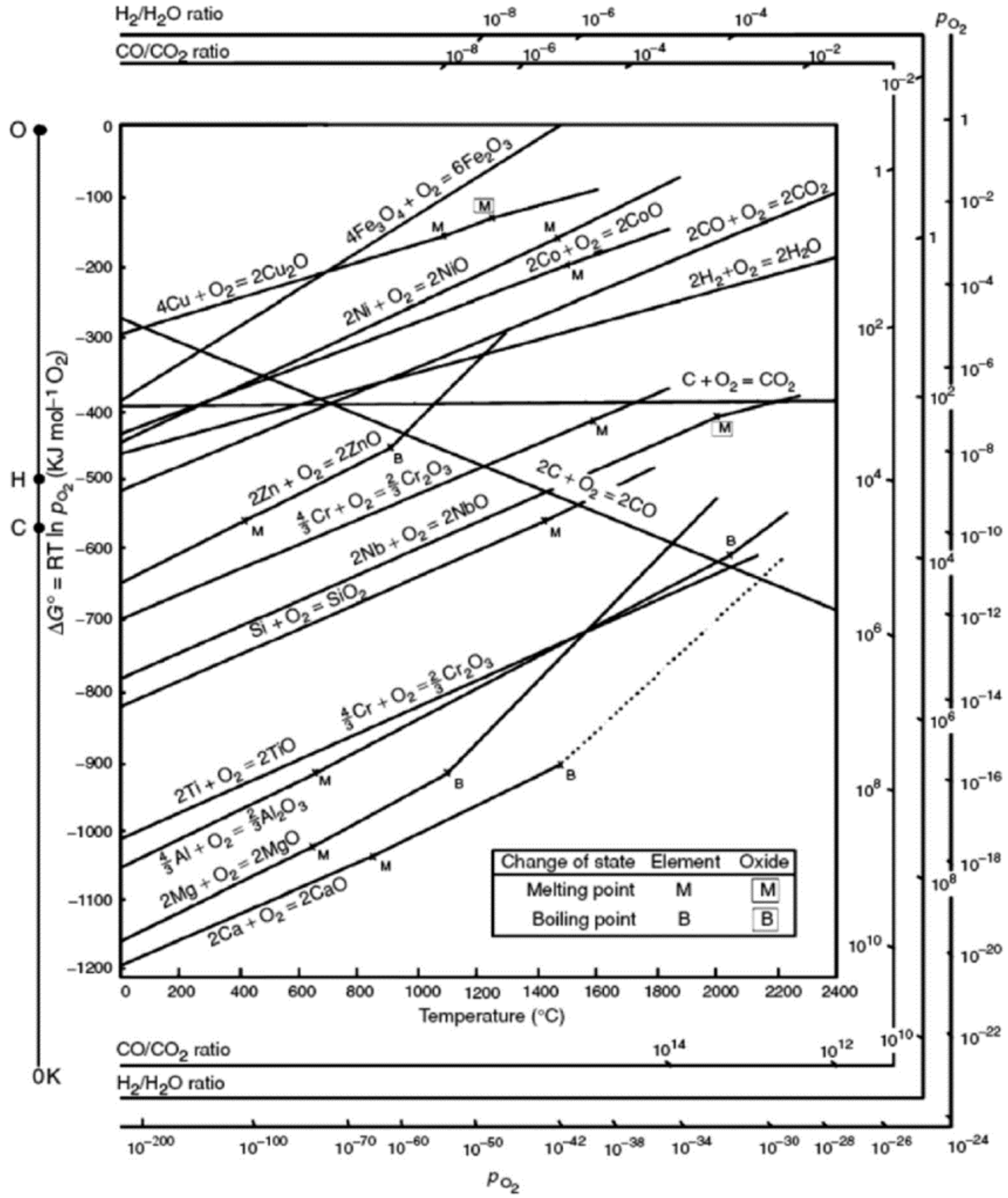

Figure 11. Ellingham diagram