SECTION A

QUESTION 1

(a) [3 marks]

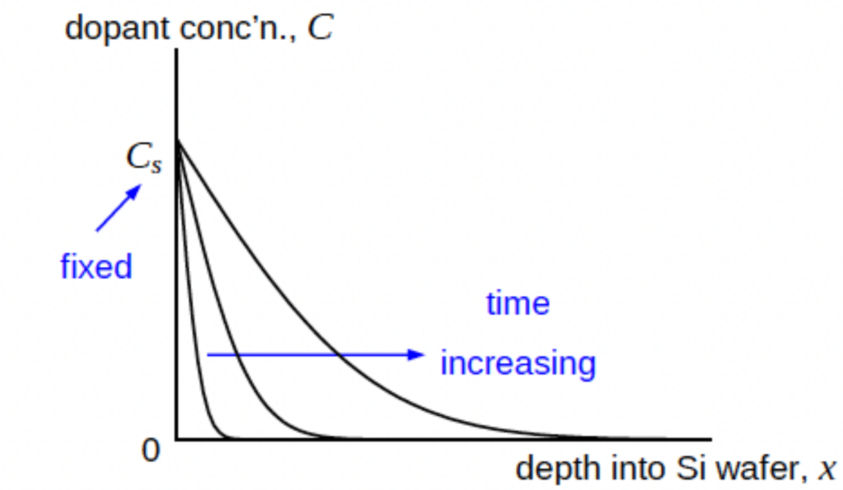
A semiconductor has both the characteristics of a conductor and an insulator. Pure silicon is an insulator and does not conduct electricity, but adding chemical ions, as impurities, enables the silicon to conduct current.

The aim of doping is to produce a near-uniform distribution of dopant, at a defined depth, in the silicon. **Pre-deposition** sets the amount of dopant; **drive-in** spreads the dopant across the material.

(b) [7 marks]

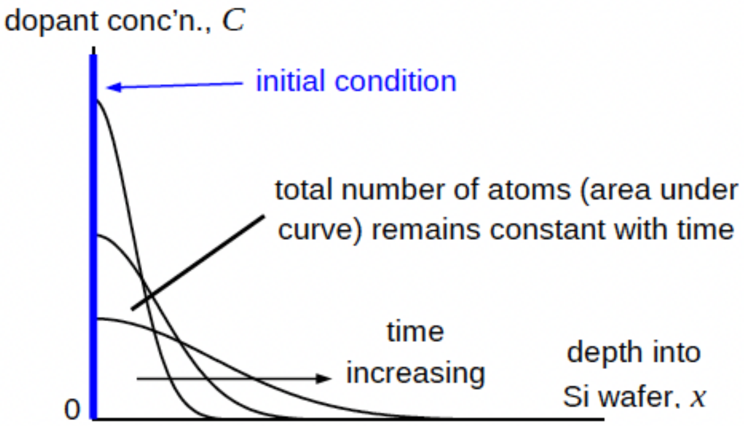
Pre-deposition
The surface concentration of the dopant remains constant throughout the pre-deposition process, and the initial concentration in the silicon substrate is zero.

$$C(x, 0) = 0; \quad C(0, t) = C_0; \quad C(\infty, t) = 0$$



Drive-in
The dopant is removed from the surface of the silicon substrate. The pre-deposited atoms are dissolved in a thin surface layer. Therefore, the number of dopant atoms in the silicon substrate remain constant and the dopant is assumed to be a delta function at the start of the process.

$$C(x, 0) = 0, \, x > 0; \quad C(\infty, t) = 0; \quad \int_0^\infty C(x,t)dx = K = \text{constant}$$



The purpose of the drive-in stage is to flatten out the distribution of dopant from the pre-deposition stage. Typically a pre-deposition stage is followed by a drive-in stage with a much larger diffusion length $\sqrt{Dt}$.

(c) [7 marks]

First, find the number of dopant atoms per unit area K by rearranging

$$C(x,t) = \frac{K}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right) \qquad \Rightarrow \qquad K = C\sqrt{\pi D t}\,\exp\left(\frac{x^2}{4Dt}\right)$$

where $C = 10^{17}$ atoms cm^{-3}, $D = 1.2 \times 10^{-12}$ cm^{2}s^{-1}, and $x = 2.5 \times 10^{-4}$ cm.
This gives $K = 4.34 \times 10^{14}$ atoms cm^{-2}.

To find the pre-deposition time use

$$K = \frac{2}{\sqrt{\pi}} C_o \sqrt{Dt} \qquad \Rightarrow \qquad t = \left(\frac{K\sqrt{\pi}}{2C_o}\right)^2 / D$$

where $K = 4.34 \times 10^{14}$ atoms cm^{-2}, $C_o = 3.8 \times 10^{20}$ atoms cm^{-3}, and $D = 1.5 \times 10^{-15}$ cm^{2}s^{-1}.
This gives a pre-deposition time of 682s, or 11.4 minutes.

The dopant distribution at the start of the drive-in stage is assumed to be a thin layer at the surface, modelled as a delta function. For this to be true, the diffusion distance during drive-in needs to be much larger than during pre-deposition, thus validating the use of the Gaussian distribution.

$$\left(\sqrt{Dt}\right)_{drive-in} >> \left(\sqrt{Dt}\right)_{pre-deposition}$$

For this case, $6.6 \times 10^{-5} >> 1.0 \times 10^{-6}$.

(d) (i) [4 marks]

Case hardening can be achieved by two processes:

Transformation hardening involves imposing a heat source to the surface to austenise a thin layer, and then quickly cooling the layer to form martensite, which can then be tempered. Surface heating can be achieved using a flame, laser, electron gun, or induction coils, followed by air or water quenching.

Carburising involves immersing the steel in a carbon-rich atmosphere at high temperature. Carbon diffuses into the surface, increasing the hardenability, making it easier to form a layer of martensite, which can then be tempered.

Examples of case hardening include steel components used in machinery, for example, gears, bearings, tool edges, which are subjected to *high surface stresses*, due to friction and sliding contact.

(d) (ii) [4 marks]

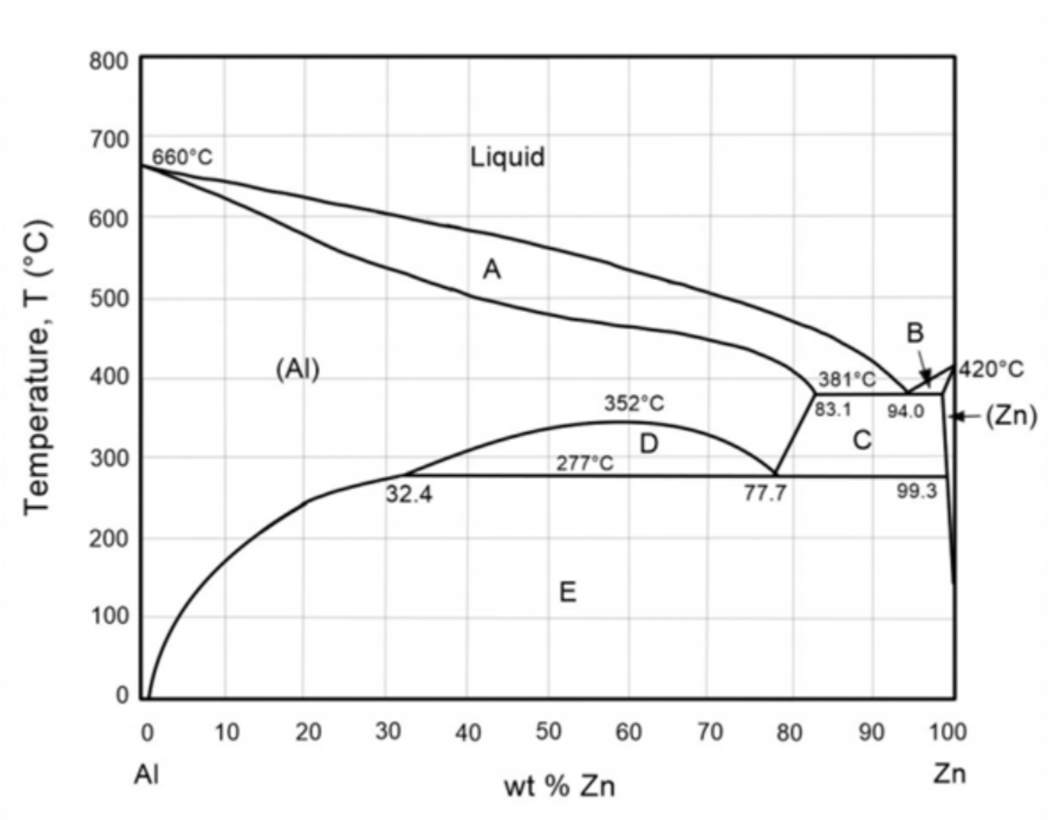
Carburising involves diffusion of the carbon into the surface of the steel, and therefore is governed by the same equations as the **pre-deposition stage** of silicon doping in semiconductors.

Whereas, for **transformation hardening** carbon is already present in the steel, and undergoes a transformation to martensite when heated. Therefore the concentration of carbon on the surface is zero. Similarly, for the **drive-in** stage of silicon doping the dopant is removed from the surface.

However, for transformation hardening the concentration of carbon in the material is assumed uniform throughout the material, whereas for the drive-in stage of silicon doping, we attempt to achieve a near-uniform distribution of dopant, at a defined depth, in the silicon, but at the start of the process the concentration profile varies as a result of the pre-deposition stage.

QUESTION 2

(a) (i) [3 marks]



A: (Al) + L

B: (Zn) + L

C: (Al) + (Zn)

D: $(Al)_1 + (Al)_2$
where both are Al solid solutions but with different levels of Zn dissolved in the solution

E: (Al) + (Zn)

(a) (ii) [3 marks]

There is a **eutectic** reaction at 381°C:

L (94 wt% Zn) → (Al) (83.1 wt% Zn) + (Zn) (~98 wt% Zn)

There is a **eutectoid** reaction at 277°C:

(Al) (77.7 wt% Zn) → (Al) (32.4 wt% Zn) + (Zn) (99.3 wt% Zn)

(b) [12 marks]

Assuming the system is at equilibrium, allowing the lever rule to be used.

First alloy at 80 wt% Zn, is cooled from solid and involves a eutectoid reaction.

At 380°C: single-phase stable (Al) solid, composition 80 wt% Zn.

From ~325°C to 277°C: As the temperature drops grains of (Zn) start to form at ~95 wt% Zn on the grain boundaries of the (Al) solid, increasing to 99.3 wt% Zn at 277°C. The remaining (Al) solid changes composition from 80 wt% Zn at ~325°C down to 77.7 wt% Zn at 277°C.

The proportions of (Al) and (Zn) phases just above 277°C, using the lever rule are:

(Al) = (99.3 – 80) / (99.3 – 77.7) = 89.4%

(Zn) = (80 – 77.7) / (99.3 – 77.7) = 10.6%

At 277°C: The eutectoid reaction takes place, converting the remaining (Al) solid:

(Al) (77.7 wt% Zn) → (Al) (32.4 wt% Zn) + (Zn) (99.3 wt% Zn)

Below 277°C: The (Al) phase may precipitate out Zn as the concentration falls from 32.4 wt% Zn to ~1 wt% Zn, if the thermodynamics allows diffusion to occur. Note, Al-Zn is a non-heat-treatable aluminium alloy, implying that diffusion at lower temperatures is limited.

Second alloy at 90 wt% Zn is cooled from liquid and involves the eutectic reaction.

At 480°C: single-phase stable liquid, composition 90 wt% Zn.

From ~420°C to 381°C: As the temperature drops grains of (Al) nucleate and grow from the liquid, starting at at ~75 wt% Zn and increasing along the solidus line to 83.1 wt% Zn. At the same time the concentration of the liquid follows the liquidous line, from 90 wt% Zn to 94 wt% Zn, to maintain the overall concentration of the mixture.

The proportions of (Al) and L phases just above 381°C, using the lever rule are:

(Al) = (94.0 – 90) / (94.0 – 83.1) = 36.7%

L = (90 – 83.1) / (94.0 – 83.1) = 63.3%

At 381°C: The eutectic reaction takes place, converting the remaining L solid:

L (94.0 wt% Zn) → (Al) (83.1 wt% Zn) + (Zn) (~98% Zn)

Below 381°C: The (Al) phase may precipitate out Zn, particularly below 277°C, as the concentration falls from 32.4 wt% Zn to ~1 wt% Zn, if the thermodynamics allows diffusion to occur.

(c) (i) [1 marks]

During solution heat treatment, the alloy must reach a homogenous single phase microstructure, with the solute atoms uniformly distributed in the matrix phase. Suitable temperatures for solution treatment for each alloy are:

Al – 4 wt% Cu: ~500°C, within the α region

(c) (i) [6 marks]

After slow cooling: to room temperature, the precipitates have time to nucleate and grow, since the required diffusion processes can occur more easily and quickly at higher temperatures. This generate course precipitates which provide only minor impeding of dislocation motions, and therefore the allows are not strengthen.

The Al – Mg alloy (100 MPa) and the Al – Cu alloy (100 MPa) have similar yield strengths after slow cooling to room temperature, as the contain fractions solute, providing increase solid solution hardening.

The weight fractions of precipitates in the Al – Cu alloy, using the lever rule are:

Al – 4 wt% Cu: = (4 – 0) / (54 – 0) = 7.4%

There is no phase diagram is available for the Al – Mg alloy in the Materials databook, but we can assume the fraction of solute is similar to the Al- Cul alloy.

Following quenching and reheating:
Al – Cu alloys are heat treatable, at concentrations up to about 5 wt% Cu, with the phase diagram showing the solubility of Cu in Al, which allows the Cu to be trapped in a supersaturated solid solution upon quenching, and reheated to form a fine array of Al–Cu precipitates, and a strengthened and hardened alloy (at 350 MPa). This process involves:

- Solution heat treatment of the alloy (at ~500°C within the α region) to allow the Cu to enter into solution.
- Quenching the alloy, in a bath of cold oil or water (depending on the cooling rate), to generate a super-saturated solid solution, in which the solute (Cu) remains in solution, contrary to the equilibrium state shown on the phase diagram which shows a mixture of (Al) and θ phases.
- The quenched allow is reheated to an intermediate temperature (~200°C) smf held for 5 hours which is high enough to allow precipitation to occur, but low enough to ensure slow growth of the precipitates and create an alloy with fine precipitates. This lower temperature allows the alloy to be formed in a carefully controlled manner, giving an increased yield strength of 350 MPa.

Al – Mg alloys are non-heat treatable, meaning the thermodynamics don't allow precipitates of Al – Zn or Zn to form at lower temperatures. This means that the process of quenching and reheating provides no additional strength or hardening to the alloy, giving a yield strength of 100 MPa, which is equal to the yield strength after slow cooling.

Holding for 5 hours:

It is worth noting that heat treatment at 200°C for 5 hours may result in "over-ageing", where the alloy is softened. Over time, the precipitates diffuse through the matrix and group together to create a progressively coarser distribution, softening the alloy and undermining the age hardening progress. Eventually, if held for very long times, the alloy will revert to the equilibrium state (i.e. 100 MPa for the Al – Cu example).

QUESTION 3

(a) (i) [6 marks]

Gold is a noble metal, meaning it has very low reactivity and does not easily interact with oxygen or other atmospheric substances. It resists oxidation and does not form an oxide layer, making it highly resistant to corrosion. Except for exposure to specific acids, gold remains unaffected by moisture, oxygen, and most acids.

Aluminium is protected by a thin but strong layer of aluminium oxide (Al_2O_3), which forms when it reacts with oxygen. This oxide layer is highly stable and self-healing, meaning that if it gets scratched or damaged, it quickly reforms to maintain protection. As a result, aluminium is highly resistant to further oxidation and corrosion under normal atmospheric conditions.

Stainless steel owes its corrosion resistance to chromium, which reacts with oxygen to form a passive layer of chromium oxide (Cr_2O_3). Like aluminium, this layer is self-repairing, preventing further oxidation even if it gets damaged. Additional alloying elements like nickel and molybdenum further enhance its durability, making stainless steel highly resistant to rust and environmental degradation.

(a) (ii) [3 marks]

The three common ways which mass changes in corrosion are:

Linear gain: when the oxide stays on the metal surface but cracks/peels off and allows oxygen to reach freely the metallic surface for further oxidation

Linear loss: when the oxide does not stay at the surface (i.e. a flaky corrosion product is removed) or the corrosion product soluble and dissolved.

Parabolic gain: when the corrosion product inhibits the required species from reaching the surface of the metal so as the corrosion layer thickens and the overall rate becomes controlled by diffusion through the corrosion layer.

(a) (iii) [4 marks]

Some examples of social, economic and environmental impacts of corrosion include:

Social Impacts

1. Safety Hazards: corrosion can lead to catastrophic failures in infrastructure, such as bridges, buildings, pipelines, and transportation systems. These failures pose significant risks to public safety, leading to accidents, injuries, and loss of life.
2. Disruption of Services: corrosion-induced failures in water distribution systems, electrical grids, or transportation networks can cause widespread service disruptions, affecting daily life and public health.

3. Reduced Quality of Life: in regions where resources are scarce, the need to replace or repair corroded infrastructure diverts funds from other critical services, such as education or healthcare.

Economic Impacts

1. Direct Costs: the global cost of corrosion is estimated to be in the trillions of dollars annually, comprising expenses for repair, maintenance, and replacement of affected materials and infrastructure. Industries such as oil and gas, construction, and transportation face significant losses due to equipment downtime and productivity interruptions.
2. Indirect Costs: Corrosion-related failures can result in legal liabilities, increased insurance premiums, and loss of reputation for businesses.
3. Impact on Trade and Commerce: Corrosion of shipping vessels, containers, and transport systems can impede international trade by causing delays, damage to goods, or increased operational costs.

Environmental Impacts

1. Resource Depletion: Corrosion accelerates the consumption of natural resources as more raw materials are required to replace damaged structures and equipment. Increased mining and manufacturing to meet these demands further deplete finite resources.
2. Pollution: Corrosion-related failures in pipelines or storage tanks can lead to the release of hazardous substances (e.g., oil spills, chemical leaks) into the environment, contaminating soil, water, and air. The disposal of corroded materials contributes to landfill waste and environmental degradation.
3. Carbon Emissions: The production and transportation of replacement materials and equipment generate significant greenhouse gas emissions, exacerbating climate change.

(b) [8 marks]

Corrosion is the progressive attack of materials, typically metals, due to chemical reactions with their environment.

The fours conditions required for aqueous corrosion, with mitigation options, are:

1. **An anodic reaction:**
   The anodic reaction in corrosion is the electrochemical process where metal atoms lose electrons and dissolve into the surrounding environment as metal ions. This reaction occurs at the anode, where oxidation takes place.

   The general anodic reaction can be written as:

   $$M \rightarrow M^{n+} + ne^-$$

Where M is the metal, M^{n+} is the metal ion with a positive charge (oxidation state n), and n is the number of electrons lost by each metal atom.

For example, the anodic reaction during the corrosion of iron is

$Fe \rightarrow Fe^{2+} + 2e^-$

Corrosion prevention strategies often focus on controlling the anodic reaction, such as using inhibitors or protective coatings to reduce metal dissolution.

2. **A cathodic reaction:**

The cathodic reaction in corrosion is the electrochemical process where reduction occurs, involving the gain of electrons that are released by the anodic reaction. This reaction takes place at the cathode, which is typically a site on the metal surface or an adjacent material.

The specific cathodic reaction depends on the environmental conditions, such as the availability of oxygen, pH, and the presence of certain ions.

For example, in environments where oxygen and water are present, the cathodic reaction often involves the reduction of oxygen:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Corrosion can be mitigated by making the entire metal surface a cathode (rather than an anode) through techniques like:

- Sacrificial Anode: using a more reactive metal to corrode instead.
- Impressed Current: applying an external current to drive reduction reactions.
- Inhibitors: applying chemicals (like paint, zinc) that reduce oxygen availability or passivates the surface.

3. **A conductive path between the anodic and cathodic sites:**

Corrosion requires a conductive path between the anodic and cathodic sites to enable the flow of electrons and complete the electrochemical circuit. The electrons released from the anodic reaction must be able to travel to the cathodic site, to participate in the reduction reaction. Without a conductive path the corrosion process stops.

To mitigate corrosion, the conductive path between the anodic and cathodic sites can be disrupted:

- Coatings: insulate the metal surface to block electron flow.
- Drying: remove moisture to eliminate the electrolyte.
- Cathodic Protection: alter the electrochemical circuit to protect the structure.

4. **A solution containing ions to transport charges (i.e. an electrolyte):**

A conductive medium, typically an electrolyte (e.g., water containing dissolved salts or acids), serves as the path for ionic conduction. This enables positive metal ions (M^{n+}) to move away from the anode, and negative ions (i.e. OH^-) to move toward the anode, thus balancing the charges. This ionic movement complements the electron flow in the metal and helps sustain the overall corrosion process.

To prevent or slow down aqueous corrosion:

- Remove the Electrolyte: keeping metals dry or controlling humidity prevents the formation of an electrolyte.
- Control Ion Concentrations: using inhibitors to reduce reactive ion availability.
- Apply Protective Coatings: barriers like paints or sealants block contact between the metal and the electrolyte.

(c) [4 marks]

Passive Galvanic Cathodic Protection: is a corrosion prevention technique that uses a more reactive (less noble) metal, called a sacrificial or galvanic anode, to protect a less reactive metal structure from corrosion.

The more reactive metal (the sacrificial anode) serves as the anode and undergoes oxidation (corrosion):

$$M \rightarrow M^{n+} + ne^{-}$$

The protected structure becomes the cathode, where reduction reactions occur, preventing its oxidation.

Active galvanic cathodic protection: or Impressed Current Cathodic Protection (ICCP). uses an external power source to drive the cathodic protection process.

For large structures, sacrificial anodes are costly and might fail to deliver the necessary current to protect the cathode. In these cases, the source of current can instead be provided by an external power source connected to an anode.

The anode can either be a stable anode, where the environment surrounding the anode is oxidised, or a consumable anode (e.g. scrap iron which would corrode away).

Active galvanic cathodic protection is used over **passive galvanic cathodic protection** when the natural electrochemical potential difference between the anode and the protected metal is insufficient to prevent corrosion. Active galvanic cathodic protection is therefore used for protecting large structures, in highly corrosive environments, for long-term installations, or situations requiring precise corrosion control, where natural galvanic action is enough.

SECTION B

QUESTION 4

(a) [3 marks]

Lowest: Tg + 30C, highest: -196C

(b) [5 marks]

(i) at liquid nitrogen temperature, the polymer chains have reduced mobility as they are constrained by copious secondary bonds. As a result, the material very stiff but brittle. The material's Young's modulus can be three orders of magnitude larger compared to that at higher temperatures (i.e., above T_g)

(ii) all secondary bonds are broken. The elastic response is governed by cross-links, which allow for large elastic strains

(iii) Due to entropic forces, the elastic modulus of the material increases with temperature, so it is higher at Tg + 60C than at Tg + 30C.

(c) [5 marks]

T=-196°C - No substantial difference.
T> T_g - thermoplastics show a significant drop in stiffness since they are not cross-linked and all secondary bonds have been broken.

(d) [6 marks]

By lowering the cooling rate during the manufacture of thermoplastics, it is possible to increase their degree of crystallinity and, in turn, their stiffness at temperatures above T_g. This phenomenon is related to the higher density of secondary bonds present in the densely packed crystalline regions of the slow-cooled polymer.

(e) [6 marks]

Applying loads during the manufacture of polymers results into orientation strengthening during which molecular chains are stretched and aligned along a certain direction, leading to significant increase in strength and stiffness. A process which exploits this behaviour is fibre drawing or blow moulding. One which doesn't is injection moulding.

QUESTION 5

(a) [5 marks]

We can calculate the 4 different strain rates for the experiments shown in Figures 2 and 3 by computing the gradient the lines from their start and end point:

Strain	Time [h]	Stress [Mpa]	Temperature [K]	Strain rate
0.0005	0	80	973	
0.0025	500	80	973	4.0000E-06
0.00025	0	80	888	
0.00075	650	80	888	7.6923E-07
0.0006	0	100	923	
0.0015	450	100	923	2.0000E-06
0.0002	0	50	923	
0.0007	500	50	923	1.0000E-06

(b) [8 marks]

We use the data in Fig. 3 to calculate the creep exponent n, since at constant temperature:

$$\frac{ln(\dot{\varepsilon}_{50\ MPa})}{ln(\dot{\varepsilon}_{100\ MPa})} = n \cdot \frac{ln(50\ [MPa])}{ln(100\ 50\ [MPa])}$$

Which gives

$$n = 1$$

To compute Q, we use the data in Fig. 2 since creep is a thermally activated phenomenon. We therefore input the top two strain rates listed in the answer to part (a) into the strain rate equation:

$$ln\left(\frac{\dot{\varepsilon}_{700°C}}{\dot{\varepsilon}_{615°C}}\right) = ln\left(exp\left(\frac{-Q}{R \cdot (700 + 273)}\right) / exp\left(\frac{-Q}{R \cdot (615 + 273)}\right)\right) =$$

$$ln\left(\frac{\dot{\varepsilon}_{700°C}}{\dot{\varepsilon}_{615°C}}\right) = Q \cdot \frac{973 - 888}{8.314 \cdot 973 \cdot 888}$$

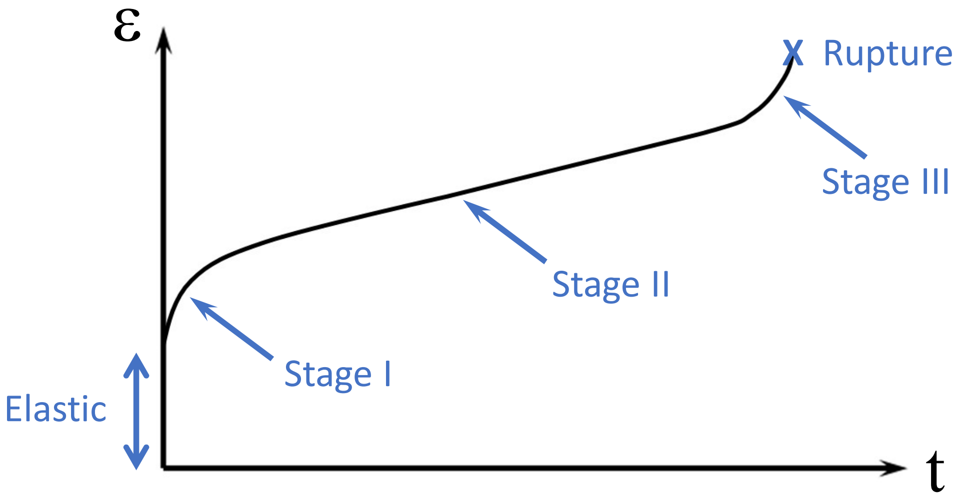
Resulting in

$$Q = 139.33\ \left[\frac{kJ}{mol}\right]$$

(c) [7 marks]

Given the result in part (b), we conclude that the material is subject to diffusional creep since n = 1. The most effective strategy to improve the creep resistance of the alloy is to precipitate harden it to reduce dislocation mobility.

(d) [5 marks]



During tertiary creep, internal flaws like voids or cracks start to form in the material, especially at internal interfaces such as grain boundaries. This leads to a significant loss of strength and eventually causes material's rupture.

QUESTION 6

(a) (i) [5 marks]

(i) TTT diagrams in steel indicate the fraction of material which undergoes a certain diffusive transformation upon cooling. They are equivalent to transformation rate diagrams when taking the inverse of time (i.e., the rate) as the x-axis. At low temperatures, the transformation rate is hindered by low kinetics of diffusion. At high temperatures, the transformation rate is limited by the little undercooling (i.e., low driving force). At intermediate temperatures, the transformation rate is maximized. This gives rise to D-shaped transformation rate diagrams, which correspond to C-shaped TTT diagrams.

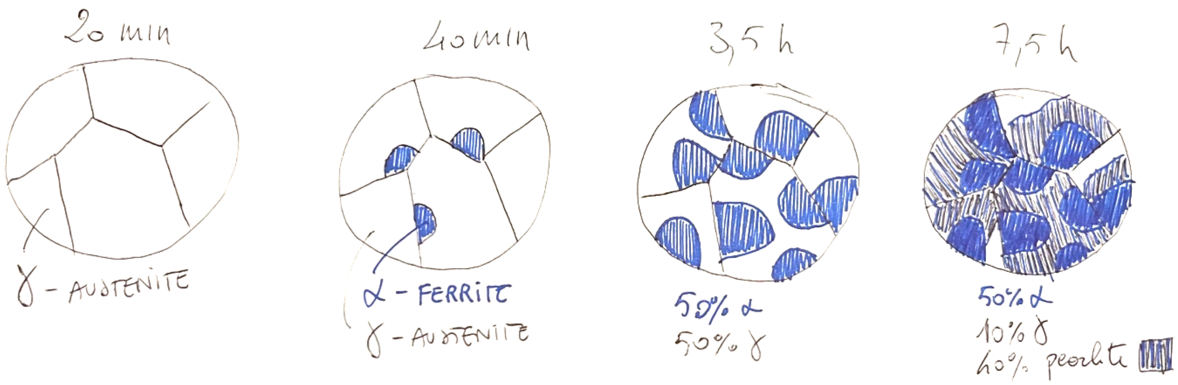
(a) (ii) [4 marks]

(ii) Transformation of austenite to martensite is diffusionless and thus is rate limited.

(b) [4 marks]

- 30% ferrite and the rest is pearlite
- Fully bainitic

(c) [6 marks]



(d) [4 marks]

“Hardenability” refers to the propensity of steel to form martensite upon cooling. The higher the hardenability, the easier it is to for martensite (rather than the more equilibrium phases such as pearlite/bainite) at lower cooling rates. The high cooling rates during welding may be conducive to the formation of martensite which is very hard but brittle and thus can lead to fast fracture in the presence of cracks.

(e) [2 marks]

Steels with high martensite content can be aged to induce the precipitation of fine carbides which greatly enhance strength without compromising on toughness.