

NATURAL SCIENCES TRIPOS Part IB  
NATURAL SCIENCES TRIPOS Part II (General)

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Monday 25 May 2009      13.30 to 16.30

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**MATERIALS SCIENCE AND METALLURGY (1)**

*Answer **five** questions, not more than **two** being chosen from any one section.*

*Write on **one** side of the paper only, and begin your answer to each question at the top of a new sheet.*

*Where questions are divided into a number of parts, the **approximate** fraction of credit allocated to each part is indicated by the percentage in the right hand margin.*

*Candidates using electronic calculators are advised to indicate clearly the sequence of steps in their working. Appropriate credit can then be given for the intermediate stages, even if the final stage is incorrect.*

*The answer to **each question** must be tied up **separately**, with its own cover-sheet.*

*Write the relevant **question number** in the square labelled 'Section'. Also, on **each** cover-sheet, list the numbers of **all** questions attempted.*

**STATIONERY REQUIREMENTS**

*Metric graph-paper*

*Blue cover sheet  $\times$  5*

*A4 script paper*

*Rough work pad*

*Tags*

**SPECIAL REQUIREMENTS**

*Data Book (supplied by Department)*

*Approved calculator allowed*

<p><b>You may not start to read the questions printed on the subsequent pages of this question paper until instructed that you may do so by the Invigilator</b></p>
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## SECTION A

## 1.

The following data were obtained on polarising nickel in an acidic solution,  $pH = 1$ : critical current density  $50 \text{ A m}^{-2}$ , passive current density  $50 \text{ mA m}^{-2}$ , passivation potential  $0.16 \text{ V (SHE)}$  and anodic Tafel slope  $0.06 \text{ V}$  per decade of current density. ‘SHE’ refers to the standard hydrogen electrode.

- (i) Plot the anodic polarisation curve for this system between the potential limits  $-0.20 \text{ V(SHE)}$  and  $+0.80 \text{ V(SHE)}$ . [20%]
- (ii) Write balanced reactions for the processes occurring in each of the regions of the curve. [15%]
- (iii) The standard chemical potential of  $\text{NiO}$  is  $-216 \text{ kJ mol}^{-1}$ , and that for  $\text{H}_2\text{O}$  is  $-237 \text{ kJ mol}^{-1}$ . Calculate the equilibrium potential between  $\text{Ni}$  and its oxide at  $pH = 1$ . Use this information to calculate the minimum anodic overpotential at which the nickel passivates in this electrolyte. [25%]
- (iv) Calculate the corrosion rate and the corrosion potential of a nickel pipe in aerated acidic solution of  $pH = 1$ , containing  $10^{-3} \text{ mol dm}^{-3}$  of dissolved oxygen, given a diffusion layer thickness of  $0.1 \text{ mm}$  and a diffusion coefficient of  $10^{-9} \text{ m}^2 \text{ s}^{-1}$ . Estimate the lifetime to perforation of a nickel pipe of wall thickness  $2 \text{ mm}$ . What would happen to the corrosion rate if oxygen is removed from the electrolyte? [40%]

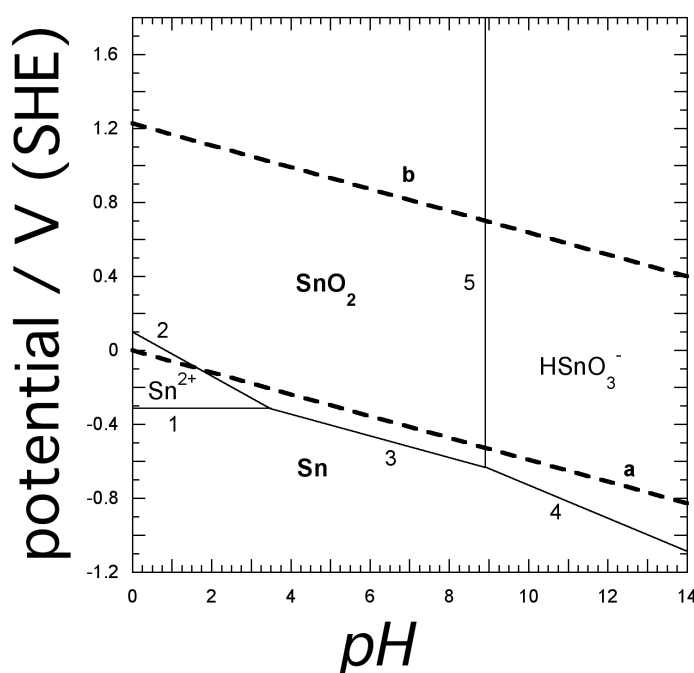
[The density of nickel is  $8900 \text{ kg m}^{-3}$  and its atomic mass is  $58.7 \text{ g mol}^{-1}$ ]

## 2.

- (i) Explain why  $\text{NiO}$  has a defect lattice. [20%]
- (ii) Explain why the addition of 1 at.% chromium to nickel reduces its oxidation resistance in air, whereas the addition of 20 at.% chromium enhances it. [20%]
- (iii) Show that the electron conductivity of  $\text{NiO} \propto p^{\frac{1}{6}}$ .  $p$  is the pressure of oxygen. [20%]
- (iv) Explain why the gradient of the metal/metal-oxide line on the Ellingham diagram increases above the melting temperature of the metal, but decreases beyond that of the oxide. [20%]
- (v) Show that the oxidation of a metal in a gaseous mixture of  $\text{H}_2$  and  $\text{H}_2\text{O}$  is equivalent to its oxidation in  $\text{O}_2$ . [20%]

3.

The simplified Pourbaix diagram below is for tin in equilibrium with water at 25°C, for a dissolved ion concentration of  $10^{-6} \text{ mol dm}^{-3}$  over the  $pH$  range 0 to 14.



- (i) Write balanced reactions for lines labelled '3', 'a' and 'b' and explain why the lines are parallel. [20%]
- (ii) Sketch a polarisation curve that might be expected from tin in a solution of  $pH = 1$ , indicating the approximate potential ranges over which immunity, corrosion and passivation occur. [15%]
- (iii) Use the Pourbaix diagram to calculate the standard chemical potential of the oxide SnO<sub>2</sub>. [30%]
- (iv) Tin has a high overpotential for hydrogen evolution. Explain what this means and its significance when using tin coatings over steel for corrosion protection. [15%]
- (v) Use the Pourbaix diagram to explain the circumstances in which tin can be used to protect the internal surfaces of steel cans containing acidic foods. [20%]

TURN OVER

## SECTION B

4.

- (i) A steel containing 0.2 wt% C and an aluminium alloy with 4 wt% Cu were each held at homologous temperatures of approximately 0.85 for 30 min and then quenched. Describe the resulting microstructures and explain how they arise. Comment on the likely mechanical properties of the alloys in the quenched condition. [30%]
- (ii) For each of these alloys, explain how a further heat treatment could be utilised to optimise the combination of strength and toughness of the as-quenched state. [40%]
- (iii) Sketch and annotate the microstructure expected in each of these alloys, in the state corresponding to the optimum combination of strength and toughness. [30%]

[An homologous temperature of a substance is the ratio of its absolute temperature to its absolute melting-temperature.]

5.

- (i) What is the Biot number, and what is its relevance when casting metallic alloys? By considering heat flow, derive an expression for the Biot number. [40%]
- (ii) Explain the basis of dendrite formation when a metallic alloy solidifies. [30%]
- (iii) Sketch and account for the expected grain structure across a sand casting made from a 60 wt% Cu, 40 wt% Ni alloy. How might the microstructure change if the alloy is die cast and what effect would this have on mechanical properties? [30%]

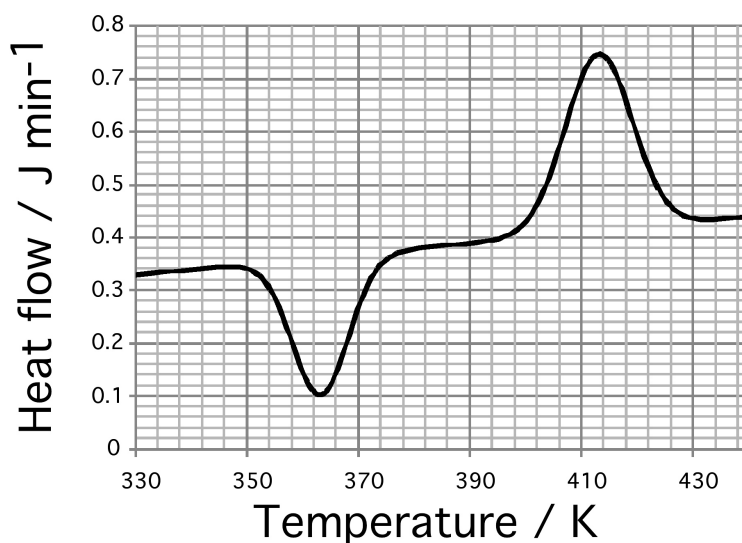
6.

- (i) By considering the flux of atoms through the lattice and through dislocation cores, derive an expression to show how the measured overall diffusion coefficient varies with dislocation density. Sketch the variation of the individual measured, lattice and dislocation-core diffusion coefficients with temperature for an annealed metallic alloy. What difference would you expect if the alloy was cold worked? [50%]
- (ii) Explain the mechanisms by which drug release from a medical pill may be controlled by the use of polymers. [50%]

## SECTION C

7.

- (i) Describe the technique of differential scanning calorimetry (DSC) and outline how it can be used to characterise the physical behaviour of polymers with reference to the glass transition and melting behaviours. Show how the area under a plot of heat flow per unit time,  $Q$ , versus absolute temperature,  $T$ , is related to the latent heat of phase transformation in the sample. [30%]
- (ii) The figure below shows a DSC trace obtained from a semi-crystalline sample of polyethylene of mass 1 mg for a heating rate of  $20 \text{ K min}^{-1}$ . The direction of positive heat flow is endothermic. By approximating the peaks by Gaussian functions, or otherwise, determine the degree of crystallinity of the original polyethylene sample by mass, stating your assumptions. [50%]



- (iii) The X-ray diffraction determined crystallinity for a similar sample was 32%. Comment on this value compared with the answer obtained above using DSC. [20%]

$$\left[ \int_{-\infty}^{\infty} a \exp\left(-\frac{(x-b)^2}{2c^2}\right) dx = ac\sqrt{2\pi}, \text{ where } a \text{ is the peak height, } c \text{ is the half-width at half-maximum and } b \text{ is the peak position. Latent heat of fusion of polyethylene} = 220 \text{ J g}^{-1} \right]$$

**TURN OVER**

8.

- (i) With the aid of diagrams, illustrate what is meant by the *conformation* of a polymer molecule, and explain how changes in conformation are related to the glass transition in disordered polymer systems. [20%]
- (ii) Polyisoprene has a glass-transition temperature  $T_g = 75^\circ\text{C}$ , whereas atactic polystyrene has  $T_g = 100^\circ\text{C}$ . Explain this difference in terms of the monomer unit structures and their effect on polymer conformation. [30%]
- (iii) In the Gaussian chain model for the conformation of a polymer above its glass transition temperature,  $T_g$ , the probability of a chain end being some distance  $r$  to  $r + dr$  from the origin is given by:

$$P(r)4\pi r^2 dr = \left(\frac{b}{\sqrt{\pi}}\right)^3 \exp(-b^2 r^2)4\pi r^2 dr \quad \text{where} \quad b = \sqrt{\frac{3}{2na^2}}$$

and  $n$  is the number of monomer segments of length  $a$ .

What is the limiting behaviour of  $P(r)$  when  $r$  becomes large and what is the significance of this in terms of the validity of the model?

Show that the root mean-squared end-to-end distance,

$$\sqrt{\langle r^2 \rangle} = \left( \int_0^\infty r^2 P(r)4\pi r^2 dr \right)^{\frac{1}{2}} = a\sqrt{n}$$

[50%]

$$\left[ \int_0^\infty x^2 \exp(-\alpha x^2) dx = \frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}} \right]$$

9.

- (i) Sketch the stress–strain curve expected for an open–cell polymeric foam, and describe how each portion of the curve relates to the structural changes occurring in the foam with increasing strain. [30%]
- (ii) For low strains, the Young’s modulus of an irregular foam,  $E^*$ , is expected to scale with relative density as follows:

$$\frac{E^*}{E_S} = C \left( \frac{\rho}{\rho_S} \right)^n$$

where  $E_S$  is the Young’s modulus of the solid material,  $\rho/\rho_S$  is the relative density of the foam, and  $C$  and  $n$  are constants. The table below shows computed data for a 3–dimensional irregular foam, assuming there is no rotation at the nodes.

$\rho/\rho_S$	$E^*/E_S$
0.01	$0.154 \times 10^{-3}$
0.02	$0.514 \times 10^{-3}$
0.04	$1.603 \times 10^{-3}$
0.08	$4.660 \times 10^{-3}$

Determine the scaling exponent  $n$  for the irregular foam, and compare this with the analytical value obtained for a 2–dimensional honeycomb foam, suggesting reasons for any difference between the two values. [70%]

**END OF PAPER**