ENGINEERING TRIPOS PART IIB - CRIB

April 2015

Module 4I5: NUCLEAR MATERIALS

ANSWER TO QUESTION 1 (marks out of 20)

Comments from assessor's report: Part (a) was generally answered well, with most students being able to give advantages and disadvantages of uranium metal and uranium dioxide. Irradiation growth was generally described well in (b), although some students discussed thermal cycling growth instead. The calculation in (c) was either done very well or very poorly. Most students stated that γ-U is cubic in (d), but only about half knew it was stabilised with alloying additions. Quite a lot of detail was missed by most students in (e).

(a) Advantages and disadvantages of uranium metal and uranium dioxide:

- UO_2 has a much higher melting temperature than U
- U has a higher density of fissile nuclides than UO_2
- Thermal conductivity of U is much higher than for UO_2
- U is ductile and can easily be formed into fuel rods, whereas UO_2 is brittle and is made into pellets by sintering
- UO_2 does not show irradiation growth or thermal cycling growth, whereas U is orthorhombic and anisotropic and shows both these effects
- U has three crystalline phases between room temperature and its melting temperature, whereas UO_2 does not show polymorphism
- Corrosion resistance is better for UO_2 than for U
- Irradiation swelling is lower for UO_2 than for U
- UO_2 can absorb volatile fission products due to the presence of an octahedral interstice at the centre of its unit cell
- UO_2 is also sintered to give some residual porosity, which can counteract swelling due to volatile fission products

[5 marks]

(b) Irradiation growth is a form of dimensional instability that occurs under irradiation without the need for an applied stress, at relatively low temperatures (~300°C). The volume of the material remains constant during irradiation growth - essentially, material is moved from one place to another, so this is different to radiation swelling.

Under a neutron flux, even single crystals of α-U show irradiation growth – this arises from the generation of dislocation loops:

- interstitial loops form on (010)
- vacancy loops form on {110}

Interstitial and vacancy loops form on different planes because of the thermal spike (i.e. local heating) and the anisotropic coefficient of thermal expansion (CTE), which is positive along the *a* and *c* axes, but negative along the *b* axis (i.e. as temperature increases, it expands along the *a* and *c* directions but shrinks in the *b* direction).

Consider the effect of heating an individual grain relative to its surroundings: it experiences tension parallel to [010] (because the CTE in that direction is negative). Interstitial atoms will then preferentially condense on (010), thereby giving an expansion to relieve the tensile stress (analagous effects occur for vacancy loops on other planes). There is therefore a net expansion parallel to [010], which is probably counter-intuitive.

If the material is polycrystalline, it will not show irradiation growth if there is no crystallographic texture (individual grains would change shape but there would be no net shape change), but irradiation growth will occur if it has preferred orientation.

[5 marks]

(c) Consider a block of material of unit area and assume that a fraction X of each plane parallel to (010) is covered by dislocation loops. If the number of dislocation loops on each plane is n, then:

$$n \times \pi r^2 = X \text{, so } n = \frac{X}{\pi r^2}$$

The dislocation length is equal to the circumference of the dislocation loops:

$$= \frac{X}{\pi r^2} \times 2\pi r = \frac{2X}{r}$$

Dislocation density is dislocation length per unit volume, so

$$\rho = \frac{\text{length}}{\text{volume}} = \frac{2X/r}{b/2 \times 1} = \frac{4X}{rb}$$

$$5 \times 10^{15} = \frac{4X}{250 \times 10^{-9} \times 5.865 \times 10^{-10}}$$

Therefore $X = 0.183 = $ **18.3%**

[6 marks]

(d) γ-U is cubic and therefore exhibits greater symmetry and does not have anisotropic coefficients of thermal expansion. γ-stabilising alloying additions such as Al, Mo and Mg can help avoid this effect.

[1 mark]

(e) ^{239}Pu is the major fissile isotope of plutonium but is only found naturally in trace quantities and is mainly produced artificially through the transmutation of ^{238}U, although it can also be recovered from spent uranium fuel in thermal reactors.

There are 6 phases of plutonium, which are only stable in limited temperature ranges. It is monoclinic at room temperature, but also has orthorhombic, fcc, bct and bcc phases, and it also readily undergoes martensitic transformations. It has a relatively low melting point of 640°C. The different phases have very different densities, so there are large volume changes during phase transitions, which is problematic.

Plutonium has a lower critical mass than uranium, and is also toxic and pyrophoric as well as being very sensitive to corrosion. Its mechanical properties depend on its phase (some phases are very brittle, but others are relatively ductile), but also on impurity and defect concentrations. It is therefore difficult to work with and it properties do not allow it to be used in pure form. A variety of alloying additions (Al, Ga, Mo, Th, Zr etc) can be added to improve its properties, but the temperature gradient in alloy fuel rods then leads to composition variation, driven by the Soret effect.

[3 marks]

ANSWER TO QUESTION 2 (marks out of 20)

Comments from assessor's report: This question was answered by all students and was generally answered well. Descriptions of stress-corrosion cracking in (a) were often quite poor, but most students answered (b) and (c) well. Some answers to (d) and (e) were very good, but often quite a bit of detail was omitted.

(a) Stress-corrosion cracking involves cracking of a material by the combined action of stress and a corrosive environment, when no corrosion or cracking would be expected if only one of these factors was operating. The stresses may be due to applied loads, residual stresses from the manufacturing process, or a combination of both.

Cracking typically occurs in two stages: initiation and propagation. Following initiation, cracks propagate at a slow rate until the stresses in the remaining material exceed the fracture stress and failure occurs. Cracks in SCC would not advance without removal of metal at the crack tip. The crack growth mechanism that is thought to be involved is anodic dissolution at the crack tip. The current density at the crack tip must significantly exceed that from the crack walls because otherwise the crack would blunt, reducing the stress at the crack tip.
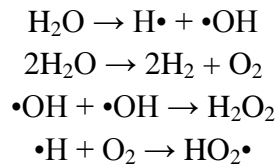
The corrosion resistance of alloys is usually largely because of a passive oxide film on their surface. Given that corrosion-resistant alloys are particularly susceptible to SCC, disruption of the passive layer is a likely cause. Plastic deformation in the metal reveals fresh metal that suffers fast corrosion before repassivation occurs. Intermediate rates of repassivation are most dangerous, because fast repassivation does not allow any significant corrosive attack whilst slow repassivation allows corrosion to blunt the crack.

A given degree of plastic flow can occur in different ways, depending on how easy it is for cross-slip to occur. In some alloys (those with high stacking fault energy), dislocations can

easily cross from one slip plane to another. In this way the deformation is rather diffuse. When the stacking fault energy is low, cross-slip is difficult; in this case slip tends to be localised on planes that have active dislocation sources or relatively low barriers to dislocation glide. The key point is that, in the latter case (i.e. when cross-slip does not readily occur), slip is more localised, and the slip steps are larger, promoting SCC.

[6 marks]

(b) Under irradiation, radiolytic decomposition of water can lead to the creation of a variety of free radicals and oxidants, through reactions such as:

$$H_2O \rightarrow H\bullet + \bullet OH$$
$$2H_2O \rightarrow 2H_2 + O_2$$
$$\bullet OH + \bullet OH \rightarrow H_2O_2$$
$$\bullet H + O_2 \rightarrow HO_2\bullet$$

These reactions raise the electrochemical corrosion potential, and can significantly increase corrosion rates.

This can be effectively countered by addition of H_2 to the water, which rapidly reacts with the oxidants: addition of only 500 ppb is sufficient to suppress the effects of radiolytic formation of oxidants. However, while this works in PWRs, it fails in BWRs. This is because in BWRs, water rises along the fuel rods, and about 25% of the way up steam starts to form. Any H_2 added to the water also boils off (i.e. it is partitioned preferentially to the steam phase) and therefore cannot remove oxidants from the water.

[4 marks]

(c) The moderator is needed in thermal reactors to slow fast neutrons into the range of thermal energy so that they have a high fission cross-section with ^{235}U. The slowing is by means of scattering off the nuclides of the moderator, and this needs to be possible without absorbing so many neutrons that the chain reaction cannot be sustained. Therefore:

- <u>Scattering cross-section</u> should be as high as possible to have the most efficient thermalisation.

- <u>Absorption cross-section</u> should be as low as possible, so that few neutrons are lost. (If the absorption cross-section is too high, the fuel may need to be further enriched, incurring further cost.)

- <u>Mass number</u> should be as low as possible because the energy transfer to a nuclide is most efficient when its mass is closest to that of the neutron ($A=1$).

[4 marks]

(d) The Wigner energy is the stored energy associated with radiation damage in graphite. The energy is associated with relatively stable, but high-energy bond configurations, for example some sp^2 and sp^3 type bonding between the graphite sheets. The damage can be annealed out by heating the irradiated graphite, but as it is annealed out, heat is released. This leads to a distinct spike in temperature, which can reach dangerous levels. Modern reactors (in contrast to the Windscale piles in which a fire caused by the Wigner energy led to a release of

radioactivity in 1957) run sufficiently warm to anneal out most of the damage in the graphite as it occurs.

[4 marks]

(e) Before irradiation, graphite's thermal expansion coefficients are highly anisotropic – it has a large positive CTE parallel to the c axis and a small negative CTE in the plane normal to c. Under irradiation, displaced atoms start to make strong bonds between the hexagonal sheets, lowering the CTE in the c direction, and the small negative CTE becomes positive. Overall, graphite becomes somewhat more isotropic as a result of being irradiated.

[2 marks]

ANSWER TO QUESTION 3 (marks out of 20)

Comments from assessor's report: The two students who attempted this question answered it well. Both achieved full marks or nearly full marks for the calculation in (c), but some detail was lacking in the descriptive parts in (a) and (b).

(a) The ion will lose energy through electronic stopping $(dE/dx)_{elec}$ interactions that depend on the electron density of the material. These are primarily ionisations that create unpaired electron defects and electron-phonon interactions that induce a localised thermal spike that may cause some displaced atoms and amorphisation if structural recovery (to crystalline form) is not fast enough and liquid state is quenched.

Electronic stopping will be the predominant stopping interaction over several μm until the ion is no longer able to promote electrons to the continuum (<100 keV). At this point the nuclear stopping $(dE/dx)_{nucl}$ becomes important and the energy is dissipated by displacing > 1000 atoms over quite a short distance ~10 nm. Thus, most of the atoms are displaced at the end of the ion track.

The energy of a recoiling heavy daughter is in the range 70-100 keV. This means that the majority of the stopping interaction with the material is nuclear. Thus, the interactions at the end of the 10 MeV Pb tracks will represent the recoil quite well. However, any damage along the track will be unrepresentative of this type of radiation damage.

[5 marks]

(b) A radioactive decay process is random, so if we assume that the distribution of ^{239}Pu is homogenous throughout the sample then, in a direct accumulation model, initially the amorphised volume will accumulate linearly.

However, as more damage accumulates there is a greater likelihood that damaged material will overlap with existing amorphised material and the damage accumulation rate is scaled by a factor (1-f), where f is the existing amorphised fraction. This leads to an equation of the form

$$V_{amorph} = V_0 \left(1 - e^{-V_i\phi}\right)$$

where f is V_{amorph}/V_o.

In a single overlap model of damage accumulation the material is able to recover a crystalline, but defect-rich area affected by the alpha decay, but a subsequent decay event will cause the collapse of overlapped areas with a critical defect concentration to go amorphous.

[5 marks]

(c)

$$\frac{V_{amorph}}{V_0} = 1 - e^{-V_i\varphi}$$

At 50% amorphous $\dfrac{V_{amorph}}{V_0} = 0.5,$ re-arrange:

$$e^{-V_i\varphi} = 1 - 0.5 \; ; \; e^{-V_i\varphi} = 0.5$$

$$\varphi = \frac{\ln 0.5}{-V_i} = \frac{\ln 0.5}{-4.25 \times 10^{-26}} = 1.631 \times 10^{25} \alpha \text{ m}^{-3}$$

Volume of 1 kg sample, say $= \dfrac{1}{4700} = 2.138 \times 10^{-4} \text{ m}^{-3}$

Total number of α to go 50% amorphous $= 2.138 \times 10^{-4} \times 1.631 \times 10^{25} = 3.487 \times 10^{21}$

Need to calculate time to accumulate 3.487×10^{21} α-decays from 1 kg 10 wt% ^{239}Pu sample

$$N_0 = \frac{100}{239} = 0.4184 \text{ mol } ^{239}\text{Pu} = 0.4184 \times 6.022 \times 10^{23} = 2.519605 \times 10^{23}$$

$$N_0 - N_{50} = 3.487 \times 10^{21} \; ; \; N_{50} = 2.519605 \times 10^{23} - 3.487 \times 10^{21} = 2.4847 \times 10^{23}$$

$$N_{50} = N_0 e^{-\lambda t} \; ; \; \ln(\frac{N_{50}}{N_0}) = -\lambda t \; ; \; t = \frac{\ln\left(\dfrac{N_{50}}{N_0}\right)}{-\lambda} = \frac{\ln\left(\dfrac{2.4847 \times 10^{23}}{2.519605 \times 10^{23}}\right)}{-2.876 \times 10^{-5}} = 484.6 \text{ years} \approx 480 \text{ years}$$

Note that answers should not be stated to too high a degree of accuracy.

[10 marks]