ANSWER TO QUESTION 1

(a) The fuel should preferably have:
- a high enough concentration (number per unit volume) of fissile nuclides (usually ^{235}U) to sustain a chain reaction,
- and therefore it is preferable to have a high concentration of sites for U atoms in the crystal structure of the fuel so that the need for enrichment of natural U is reduced.
- compatibility with plutonium (for mixed fuels).
- good formability into the shapes required for fuel (mostly rods, occasionally plates).
- good thermal conductivity (to get effective heat extraction without an excessive temperature along the centre line).
- low *growth* (i.e. change of shape) and low *swelling* under irradiation (growth and swelling may rupture the fuel cladding), and low *thermal-cycling growth*.
- low growth and low swelling should permit higher fuel burn-up, important for reducing:
  — the downtime for refuelling
  — the number of fresh nuclear fuel elements required and spent nuclear fuel elements generated while producing a given amount of energy
  — the potential for diversion of plutonium from spent fuel for use in nuclear weapons
- a high melting temperature (to run as hot as possible without melting; a higher operating temperature gives higher efficiency).
- good mechanical stability (not falling apart) under irradiation (fuel disintegration would disrupt its distribution within the cladding),
- and this implies no solid-state phase transformations within the temperature range up to the operating temperature, and an ability to absorb volatile fission products.
- good resistance to corrosion and chemical compatibility with the cladding.

(b) The key elements of thermal restructuring are:
- grain growth;
- the moving grain boundaries sweep gas from interiors, so that gas bubbles form on the boundaries and then coarsen by diffusion of the gaseous species along the boundaries themselves. This gives porosity and swelling.
- cracking — usually in a radial direction. At high temperature UO_2 is ductile, so cracking may occur mainly during reactor start-up and shut down.
- bubble/void migration up the temperature gradient to give a central void.

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(c) As UO_2 fuel is used, U is consumed and the O:metal ratio increases. As not all the excess O can combine with fission products, there is a risk of O release from the fuel, accelerating corrosion of the cladding. To avoid this, it is desirable for the starting fuel to be *hypostoichiometric* — the O:metal ratio is roughly 1.97 (not 2.00).

(d) The crystal structure of UO_2 is cubic (fluorite structure, CaF_2 archetype). This high-symmetry structure shows isotropic thermal expansion and therefore avoids the problems associated with anisotropic thermal expansion, namely *thermal-cycling growth* and *irradiation growth*. The unit cell has a large interstice in the middle; this can accommodate volatile fission products.

(e) Comparison of U metal and UO_2. (It is not expected that candidates would remember values of properties, but they should be able to make comparisons. Thus, they would not be expected to know the melting temperatures of U and UO_2, but they would be expected to know that the melting point of UO_2 is higher.) Taking the various properties in the same order as listed in part (a) above:

- U has a higher concentration (number per unit volume) of fissile nuclides than UO_2.
- UO_2 shows complete mutual solubility with PuO_2. Pu is extensively soluble in U metals. In each case, mixed fuels are possible.
- U metal shows good formability and it is not brittle. UO_2 is brittle and is made into fuel pellets by sintering of powder.
- thermal conductivity is better for U than for UO_2.
- UO_2 (having a cubic crystal structure) does not show irradiation growth nor thermal-cycling growth. (α-U, being orthorhombic, does show these effects and they pose serious reliability problems.) Irradiation swelling is much less for UO_2 than for U metal.
- UO_2 has a much higher melting temperature than U metal.
- metallic U has three crystalline polymorphs between RT and melting. UO_2 has the desirable characteristic that it does not show similar polymorphism.
- UO_2 is better than U metal at absorbing volatile fission products because of the large octahedral interstice at the centre of its unit cell. Also UO_2 is sintered to give some residual porosity; the natural annealing-out of this porosity counteracts swelling due to volatile fission products.
- UO_2 shows greater corrosion resistance, and is generally chemically more inert than metallic U. (Though the potential release of O from UO_2 is a problem that can be partially offset, as noted above, by using hypostoichiometric fuel.)

(f) The most common alternatives being considered (particularly as advanced fuels for fast-breeder reactors, FBRs) are UC and UN. Compared to UO_2, they show:

- higher concentration of fissile nuclides
- greater structural stability
- higher thermal conductivity.

Overall, they permit a higher linear heat generation rate (LHGR) and greater burn-up. UN in particular permits easier reprocessing (important for the FBR fuel cycle).

ANSWER TO QUESTION 2

(a) The cladding must:
- isolate the fuel from the coolant (this requires chemical stability, and mechanical integrity)
- have a low neutron absorption cross-section (dictates choice of elements/nuclides)
- be corrosion-resistant, and in general be compatible with the fuel and coolant
- conduct heat well (for which it may be necessary to consider heat transfer from fuel to cladding as well conduction in the cladding itself)
- have a melting point well above the operating temperature of the reactor. New designs of reactor may well have higher operating temperatures (dictates choice of alloy system, stainless steels are at present preferred for higher-temperature use)
- adequate strength and ductility, especially to withstand fuel swelling
- high stability under irradiation (the standard problems are encountered)
- low induced radioactivity (this, of course, facilitates recycling after use).

(b) The cladding is thus one of the most critical components in a reactor, and its performance (esp. irradiation growth and corrosion resistance) is often the key factor limiting attainable burn-up (a higher burn-up requiring a longer period in the reactor). The allowable time in the reactor may be limited by *swelling*, *irradiation growth* and *corrosion* of the cladding. (There are also analogous effects in the fuel, which may be significant.)

(c) The two categories of cladding alloys are:
   (i) austenitic stainless steels — used in fast-breeders reactors where the operating conditions are relatively more severe
   (ii) zirconium alloys in PWRs and BWRs.
Aspects of degradation are:

(i) Formation of dislocation loops
Irradiation displaces atoms generating vacancies and self-interstitial atoms (SIAs). These can condense to form dislocation loops that harden the material:
- the yield stress (YS) and UTS both rise, but the YS rises faster, so that the two values approach each other
- there is loss of ductility and embrittlement
- the loops in austenitic stainless steels are predominantly *intrinsic* (formed from vacancies; in Zr alloys, there are roughly equal populations of intrinsic and extrinsic (vacancy and interstitial) loops

(ii) Voids and swelling

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A problem with austenitic stainless steels. The nickel necessarily in the alloys undergoes transmutation reactions generating α particles. The helium plays a key role in nucleating voids (*gas-assisted nucleation*) and accumulation of vacancies gives severe swelling. The swelling in turn leads to accelerated creep, softening, and ultimately catastrophic weakening. The net flux of vacancies into growing voids gives Ni-rich regions around the voids and Cr- and Fe-rich further away (the *inverse Kirkendall effect*); ultimately, the composition changes cause phase instability leading to coexistence of austenitic and ferritic material.

(iii) Stress-corrosion cracking (SCC)

A problem with austenitic stainless steels, where their optimization for general corrosion resistance makes them particularly susceptible to SCC. Irradiation-assisted SCC has its origins in radiolysis of water, and in persistent effects due to microstructural changes:

— grain-boundary segregation (inverse Kirkendall effect as the boundaries act as sinks for vacancies)

— solute depletion through formation of precipitates)

— localization of strain in dislocation channels (promotes grain-boundary sliding and is effective in rupturing the passive oxide film)

— increased stresses.

(Might also note that Zr alloys do show degradation of their corrosion resistance under irradiation — this is associated with the dissolution of precipitate particles and reprecipitation in different forms, changing matrix compositions.)

(iv) Irradiation growth (i.e. change of shape):

Zirconium alloys are used in the temperature range where the matrix is hexagonal (α phase); the low symmetry (anisotropy) leads to a number of effects:

▪ the thermal expansion of α is strongly anisotropic, that parallel to the hexagonal axis (i.e. [0001], z axis, c lattice parameter] being twice that in the *basal plane* (to which the [0001] axis is normal]; thus in a locally hot displacement cascade, the main compressive stress is parallel to [0001]

▪ as a result, there is preferential formation of vacancy loops on the $\langle c \rangle$ planes (i.e. the basal planes perpendicular to [0001], and of interstitial dislocation loops on $\langle a \rangle$ planes (i.e. the prismatic planes parallel to [0001] whose normals lie in the basal plane)

▪ this non-random orientation of the different types of loops leads to *irradiation growth* in which a single crystal (each grain) changes shape under irradiation, contracting parallel to [0001] and expanding in the basal plane

▪ zircaloys are processed by hot-rolling; this gives a strong crystallographic texture (i.e. preferred orientation), and growth of individual grains therefore gives overall growth of a polycrystalline component

- the tubes used for cladding increase in length, and their diameter and wall thickness decrease; this distortion limits the attainable burn-up.

Briefly explain the process by which actinides and fission products are separated in the reprocessing of nuclear fuel. State the advantages of separating the two types of radionuclides produced during the operation of a fission reactor in terms of the disposal of nuclear waste.

Actinides and fission products are separated using the PUREX process. Nuclear fuel rods are 'hulled' to remove the zircalloy clad and then the ceramic fuel is dissolved in nitric acid. Liquid-liquid phase separation is employed using kerosene and tri-butyl phosphate (TBP) to chelate the plutonium and uranium and remove them into the organic phase. Further reduction of Pu^{4+} to Pu^{3+} allows separation of U and Pu.

Thus, reprocessing allows the separation of the most long-lived radionuclides (actinides) from the SNF. Fission products in the acidic fraction are calcined to a dry powder and vitrified with a glass frit and disposed, U and Pu can be re-used. Thus, the radiological dose to the biosphere will be significantly reduced because the radioactivity of the vitrified FP fraction falls below that of mined uranium (arbitrary benchmark) before the failure of engineered controls within the repository. [Some minor actinides (^{241}Am, ^{244}Cm) and the FP isotopes ^{99}Tc and ^{135}Cs ($t_{1/2}$ ~ 200,000 years) remain problematic].

[25%]

SYNROC is a concept for the disposal of nuclear waste. Explain the concept and indicate how the material is processed and what the final products are. How are changes in waste stream accommodated within the SYNROC concept and what is the major factor that leads it to have superior aqueous durability to borosilicate glass?

SYNROC involves the chemical incorporation of a nuclear waste stream by the ceramic fabrication of a mineral assemblage based on three phases: hollandite, perovskite and zirconolite, which are all titanates that exhibit some radiation resistance and actinide retention in nature. The oxide feed contains an excess of TiO_2, which does not from solid solution with the actinides or fission products, but allows the relative amounts of each phase to vary and thus supports variations in the waste stream composition. The primary method of production is through hot isostatic pressing (HIP), which provides a nearly 100% dense and highly insoluble product.

[30%]

The pyrochlore structure is closely related to one of the mineral phases in SYNROC. This caused a $Ca_2Ti_2O_7$ based pyrochlore to be chosen as a tailored ceramic in the *Swords to Ploughshares* options programme to dispose of weapons plutonium (^{239}Pu). Suggest an experiment to test the suitability of this material for the disposal of plutonium. If the plutonium were kept in the +3 oxidation state, describe how the composition could be adjusted to maintain the pyrochlore structure. If the long-term durability needed to be tested for 10,000 years with a 10 wt% Pu loading, describe an experiment that could test this on a laboratory time scale and how long would it take?

[45%]

[$t_{1/2}$ (^{239}Pu) = 24,100 years, $t_{1/2}$(^{238}Pu) = 87.7 years]

Solid solution could be tested by fabrication of materials with different levels of ^{239}Pu and radiation resistance by fabrication of a ^{238}Pu sample. Because of ionic radius considerations Pu will enter the structure in the Ca site; a charge balancing substitution e.g. $Na^+ + Pu^{3+} => 2Ca^{2+}$ should be used.

Add 10wt% ^{238}Pu in solid solution and monitor macroscopic swelling (density,) X-ray diffraction strain & unit cell swelling.

$$\lambda_{239} = \frac{\ln(2)}{t_{1/2}} = \frac{0.693}{24100} = 2.876 \text{ x } 10^{-5} \text{year}^{-1}$$

$$\frac{0.1}{239} = 4.184 \text{ x } 10^{-4} \text{moles} = 4.184 \text{ x } 10^{-4} \text{x } 6.026 \text{ x } 10^{23} \text{ atoms } ^{239}\text{Pu} = 2.519 \text{ x } 10^{20} = N_0$$

$$N_{10000} = N_0 \exp(-\lambda_{239} 10000) = 1.889 \text{ x } 10^{20}$$

$$N_0 - N_{10000} = 6.295 \text{ x } 10^{19} \alpha\text{-events/g}$$

$$1.889 \text{ x } 10^{20} = 2.519 \text{ x } 10^{20} \exp(-\lambda_{238} t_{238})$$

$$\lambda_{238} = \frac{\ln(2)}{t_{1/2}} = \frac{0.693}{87.7} = 7.902 \text{ x } 10^{-3} \text{year}^{-1}$$

$$\exp(-7.902 \text{ x } 10^{-3} t_{238}) = \frac{1.889 \text{ x } 10^{20}}{2.519 \text{ x } 10^{20}} = 0.7499$$

$$t_{238} = \frac{\ln(0.7499)}{-7.902 \text{ x } 10^{-3}} = 36.4 \text{ years}$$