

## Materials for nuclear reactors

The development of nuclear power in the last fifty years has involved the use of many materials – metals, alloys, ceramics, liquids and gases – which in pre-nuclear power years were relatively unknown to engineers and little used in engineering. Now these materials are becoming well known, and although not exactly commonplace, they are part of the vast range of materials used in engineering today.

It is the purpose of this chapter to give brief and qualitative description of the materials which have acquired special importance in nuclear engineering, describing their properties and the role that they play in nuclear reactor technology.

The physical characteristics of materials are of considerable importance in determining their use in nuclear reactors. Characteristics such as strength, hardness, ductility, melting point, boiling point, density and thermal conductivity are all familiar to engineers in their choice of materials for particular applications. Not so well known (before the advent of nuclear power) was the neutron cross-section, which is of crucial importance in the selection of most materials for use in the core of nuclear reactors. Most components of a reactor are subjected to high temperatures and stresses, and their properties under such conditions must be taken into consideration.

It is also necessary to have an understanding of any possible chemical reactions that may occur between materials in a reactor. For example, the coolant comes into contact at high temperature with several other components of the reactor and heat exchangers, and any possible reactions such as corrosion involving these components must be well understood.

One type of change affecting materials in reactors which is not familiar in non-nuclear applications is radiation damage. This is the name for changes which can be caused to the molecular and crystalline structure of a material as a result of its being exposed in a neutron flux, particularly a fast neutron flux, for prolonged periods. Equally, structural damage can be caused within the fuel of a reactor as a result of bombardment of individual atoms by high energy fission products. Radiation damage causes the displacement of individual atoms within the crystals of a material and changes the crystalline structure; this effect may be anisotropic, leading to expansion along some

axes and contraction along others. The results of this damage may include cracking, swelling and creep as well as changes in other properties such as ductility, hardness, strength and thermal conductivity. These results are usually only of significance after long periods of irradiation, and much research and testing in materials testing reactors, extending over several years, is needed to determine the nature and extent of radiation induced damage.

It is possible to list a number of criteria by which reactor materials may be compared and selected. These criteria include the following:

1. Good mechanical properties including (where necessary) high thermal conductivity, specific heat, density, strength, ductility, melting or boiling point and low coefficient of expansion.
2. Low neutron capture cross-section is necessary for all materials in the core except the fuel and the control rods (and burnable poisons if used).
3. Chemical stability of all materials at the operating temperatures and pressures of the reactor. No risk of oxidation, decomposition, explosion or other chemical reaction.
4. No metallurgical phase changes at operating temperatures that may lead to dimensional changes.
5. Resistance to significant radiation damage within the lifetime of the material in the reactor.
6. Materials chosen should be readily obtainable in a pure form, cheap, easy to fabricate and non-toxic.

### 10.1 Fuels

#### *Uranium*

Uranium in one form or another is by far the most common fuel material for nuclear reactors. (By comparison, the use of thorium and plutonium has so far been on a very small scale.) It can be used either as pure uranium, a metal, or as a compound such as uranium dioxide  $UO_2$  or uranium carbide UC.

Uranium is a rather soft and ductile metal which oxidizes readily in air and water at high temperature. Its melting point is  $1133^\circ\text{C}$ . It exists in one of three allotropic forms, depending on its temperature. These three different forms are called the alpha, beta and gamma phases, and changes from one phase to another due to temperature changes are accompanied by density changes. Alpha phase uranium has a density of  $19\text{ g/cm}^3$  and a thermal conductivity which varies from  $25\text{ W/mK}$  at  $25^\circ\text{C}$  to  $42\text{ W/mK}$  at  $665^\circ\text{C}$ . The transition from the alpha to the beta phase takes place at  $665^\circ\text{C}$  and is accompanied by dimensional changes in the crystalline structure of the uranium, expansion along one axis and contraction along the

others. To avoid distortion due to these anisotropic dimensional changes 665°C is considered to be the maximum operating temperature for uranium.

Metallic uranium is also very susceptible to radiation damage which produces dimensional changes and swelling above about 450°C. Consequently high burnups of metallic uranium fuel are not possible. In the British gas-cooled Magnox reactors, which are the principal users of this type of fuel, the burnup is limited to about 3500 MWd/t.

To summarize, the low operating temperature, susceptibility to radiation damage and low permissible burnup of uranium are serious disadvantages to its choice as a reactor fuel, and account for its very limited use.

Uranium dioxide  $\text{UO}_2$  is a black powder which can be fabricated by cold pressing and sintering at high temperature to produce small cylindrical pellets, and in this form it is by far the most common material for the fuel of commercial reactors. In this ceramic form  $\text{UO}_2$  has good stability at high temperature and good resistance to radiation damage which enables it to be used to high burnups. The melting point is 2865°C and the theoretical density is 10.96 g/cm<sup>3</sup>, although in practice the density of  $\text{UO}_2$  pellets produced as described above is about 10 g/cm<sup>3</sup>. The thermal conductivity is low, being about 2.5 W/mK in the temperature range from 1000 to 2000°C, however this low thermal conductivity is compensated for by the very high melting point which permits high maximum fuel temperatures.

Uranium dioxide does not react with water at high temperatures, a very valuable characteristic as otherwise cladding failures in water cooled reactors would lead to serious reactions. It can retain a large fraction of the gaseous fission products at temperatures below 1000°C, but as the fuel temperature at the centre of a pellet is likely to be greatly in excess of this value, provision must be made for fission product gas release. This is usually done by having an empty space at the top of each fuel tube into which the gases can diffuse.

During operation in a reactor  $\text{UO}_2$  pellets suffer structural changes, principally as a result of the high operating temperatures and high temperature gradients, but also as a result of prolonged irradiation. The effects may include swelling, formation of cracks and voids in the pellet and changes in the grain structure of the  $\text{UO}_2$ . This type of fuel is normally subjected to much higher burnups than pure uranium, and 5 per cent or more of the original uranium atoms in the fuel may undergo fission and be changed, each one to two intermediate mass fission product atoms.

Uranium carbide,  $\text{UC}$ , is another ceramic fuel of possible interest, but it has not been developed or used to anything like the same extent as  $\text{UO}_2$ . It may have some advantages over  $\text{UO}_2$ , principally its higher thermal conductivity and higher density which leads to more uranium atoms per unit volume of fuel, which is an advantage in a reactor. Uranium carbide reacts with water, which makes it unsuitable for use in water cooled reactors,

but it does not react with sodium below 500°C, so it might be used in fast reactors. Its melting point, 2380°C, is rather lower than that of  $\text{UO}_2$ , but this is compensated for by its higher thermal conductivity. The development of uranium carbide so far has been principally as the fuel for high temperature gas-cooled reactors.

### *Plutonium*

Pure plutonium metal is not suitable as a reactor fuel due to the large number of crystalline phases which exist up to its melting point of 640°C. The thermal conductivity is also very low, about 4.2 W/mK at room temperature. Plutonium metal is highly reactive in moist air, but it can be stored in dry air at low temperature. It is a very dangerous material, being radioactive, toxic and an essential component of nuclear weapons, and is potentially a serious health hazard, particularly if it exists as dust in the atmosphere and is taken into the lungs by inhalation.

As a reactor fuel plutonium is used as the oxide  $\text{PuO}_2$ . Its melting point is 2400°C. Plutonium dioxide is mixed with uranium dioxide to form mixed oxide fuel (MOX) which for fast reactors typically contains 20 to 25 per cent of  $\text{PuO}_2$ . The properties of this mixed oxide fuel are similar to those of  $\text{UO}_2$  alone.

### *Thorium*

Thorium has not been used as a reactor fuel to any great extent yet except in a few high temperature gas-cooled reactors. Thorium 232 is the fertile isotope from which uranium 233 is produced as described in Chapter 3, and it is theoretically possible to obtain high breeding ratios in thermal as well as fast reactors using this combination.

Pure metallic thorium has a melting point of about 1700°C. It is superior to uranium due to its better stability, but it is not used as a fuel in its pure form. Instead it is used either as thorium dioxide  $\text{ThO}_2$  or thorium carbide  $\text{ThC}_2$ . To date these compounds have only been used to a very small extent in a few high temperature gas-cooled reactors.

Thorium dioxide is similar in many respects to uranium dioxide. It is produced by the same methods of powder metallurgy, and it is chemically inert and has a good resistance to radiation damage. Thorium carbide has been used in the form of coated particle fuel in HTGRs. Very small spherical particles less than 1 mm diameter of mixed  $\text{ThC}_2$  and  $\text{UC}$ , (highly enriched in  $^{235}\text{U}$ ) are coated with thin layers of pyrolytic carbon and silicon carbide to retain fission products. These particles are dispersed in graphite to form a homogeneous mixture of fuel and moderator which has a very high operating temperature and good resistance to radiation damage.

**10.2 Moderators**

The requirements of the moderator for a thermal reactor, namely low mass number, very low neutron capture cross-section and high scattering cross-section, limit the choice to only a few materials. Hydrogen and its isotope deuterium, carbon and beryllium are the only elements that are suitable. Hydrogen and deuterium, being gases, are not sufficiently dense and must be used in the form of compounds, water and heavy water being the obvious choices. The use of hydrocarbon compounds has been tried, but has not been successful and such materials are not used as moderators. It is interesting to recall, however, that Fermi used paraffin wax in his early experiments in the 1930s to slow down neutrons and study their interactions with the elements, so he was one of the first scientists to be aware of the effects of neutron moderation.

Beryllium has a very low neutron capture cross-section (0.009 barns), high melting point (about 1300°C) and good strength, and at one time it seemed possible that it would find an application either as the moderator or the fuel cladding in thermal reactors. However, it and its compounds are toxic, and beryllium itself has low ductility and poor corrosion resistance. Beryllium oxide BeO also has undesirable properties. As a result of this neither beryllium nor its oxide have found any use in power reactors, and it is unlikely that they will be used in the future.

The choice of moderators for thermal reactors is thus limited to three materials — water, heavy water and carbon in the form of graphite.

*Water*

Water is an obvious choice for the moderator of a thermal reactor, and it can also serve as the coolant. It has excellent neutron slowing down properties which enable water moderated reactors to have much more compact cores than are possible in other types of thermal reactors. The capture cross-section of water is rather high (0.66 barns per molecule) so that water moderated and cooled reactors require enriched uranium for criticality. It is, of course, abundant, cheap and easily obtainable with high purity.

The main problem associated with the use of water as the moderator and coolant in a power reactor concerns its rather unfavourable thermodynamic characteristics. The saturation pressure and temperature relationship is such that high pressures are required to prevent boiling at high temperatures, e.g. a pressure of 150 bar is required to allow water to reach a temperature of 340°C without boiling. Pressures of 150 to 160 bar are typical of pressurized water reactors, in which the water temperature is limited to about 325°C.

It is important to maintain water purity in a water cooled and moderated reactor, firstly to minimize corrosion and secondly to prevent the water from

becoming radioactive due to ( $n, \gamma$ ) reactions with the impurities as the water flows through the reactor core. Radiation levels in the water can influence the radiation dose levels to which power station operating and maintenance staff are exposed, and the maintenance of high water purity assists in reducing operator exposures.

*Heavy water*

Heavy water is similar to ordinary water in most of its physical and thermodynamic properties. The principal difference is that deuterium has a much lower capture cross-section than hydrogen, and the capture cross-section of heavy water is only 0.001 barns. Deuterium is, however, not such a good moderator as hydrogen. Consequently, heavy water moderated and cooled reactors use natural uranium as their fuel, but their core sizes are rather larger than water moderated reactor cores. An important difference is that heavy water is very expensive to produce by separation from ordinary water, and losses by leakage must be minimized.

*Graphite*

The world's first nuclear reactor, CP-1, (Chicago Pile 1) was moderated with graphite, and although this material has not been used subsequently in American commercial power reactors, it has been used extensively in British reactors. Its nuclear characteristics, i.e. slowing down power and capture cross-section are not as good as those of heavy water, but it is readily obtainable in a pure form at reasonable cost and is easily machined. Its structural and thermal properties are good although it reacts with oxygen and air at high temperatures. Graphite has a high thermal conductivity (130–190 W/mK) and it sublimates at 3650°C without melting, so there is for all practical purposes no limit on its maximum operating temperature. Graphite cores are assembled from large numbers (many thousands) of blocks of rectangular shape in which holes are provided for fuel elements and control rods.

The effect of prolonged neutron irradiation on graphite is very important, as such irradiation causes dimensional changes and the buildup of stored energy within the crystalline structure. The dimensional changes are due to the anisotropic crystalline structure of graphite, and they depend on its temperature during irradiation. Below 300°C there is a contraction along one axis and expansion along another. At higher temperatures there is contraction in all directions. The design of a graphite core and the keys which hold one block in position relative to its neighbours must make these dimensional changes possible without damage or distortion of the core.

The stored energy, sometimes called Wigner energy, is due to the energy required to displace atoms in the graphite's crystalline structure. Neutron

irradiation causes the displacement of atoms, and if they do not return to their original positions, this energy remains stored in the graphite. This is the case at temperatures below 100°C. At higher temperatures partial self-annealing of the graphite takes place and some of the stored energy is released. It is necessary to release the stored energy in a controlled way otherwise, if it is released too rapidly, the graphite temperature can rise disastrously. This occurred at one of Britain's two original air-cooled plutonium producing reactors at Windscale, Cumbria in 1957. On that occasion an uncontrolled Wigner energy release caused the graphite temperature to reach such a high level that the graphite burned and the core of the reactor was destroyed.

Present British gas-cooled reactors operate with graphite temperatures of about 400°C at which there is continuous self-annealing of the Wigner strain energy, and no possibility exists of a repeat of the Windscale accident.

### 10.3 Coolants

The principal requirements of the coolant for a nuclear reactor are as follows:

1. Good thermodynamic properties, namely high thermal conductivity, density and specific heat, and low viscosity.
2. Chemically non-reactive with other components of the reactor.
3. Very low neutron capture cross-section.
4. It should not become radioactive as a result of ( $n, \gamma$ ) reactions which may occur when the coolant is passing through the core of the reactor.

Among the gaseous coolants, some can be eliminated from consideration for one reason or another. Oxygen and hydrogen are both reactive, the latter explosively so. Nitrogen has a significant capture cross-section (1.8 barns). Air, being a mixture of oxygen and nitrogen can also be ruled out. Oxygen 16 undergoes an ( $n, \rho$ ) reaction with high energy neutrons (e.g. fission neutrons) to form nitrogen 16 which is radioactive, but its half-life is only 7 seconds, so the radioactive hazard is short-lived. The two most suitable gaseous coolants are carbon dioxide and helium.

Carbon dioxide is a fairly unreactive gas, but it does react at high temperatures with certain types of steel and with graphite. Both these reactions have proved troublesome in British gas-cooled reactors in which carbon dioxide has been chosen as the coolant. Its advantages are its inertness, availability and cheapness, and the very low capture cross-sections of both carbon and oxygen. Carbon 13, which is a very small constituent of naturally occurring carbon, captures neutrons to a very small extent to form radioactive carbon 14 which poses a minor hazard if carbon dioxide leaks or is vented from a reactor to the atmosphere.

Helium is inert, has good thermodynamic properties and does not pose a radioactive hazard, so it might be regarded as the ideal gaseous reactor

coolant. Unfortunately, it is not readily available in large quantities and is expensive. Its use as a reactor coolant is at present confined to the few high temperature gas-cooled reactors operating in the USA and West Germany.

The properties of water and heavy water as reactor coolants have been described in the preceding section, but their moderating ability makes them unsuitable for use as coolants in fast reactors.

Liquid metals are potentially excellent reactor coolants because of their good thermodynamic properties, in particular their high thermal conductivity which leads to very good heat transfer coefficients. Sodium, lithium, mercury and sodium-potassium alloys are all possibilities, but of these only sodium has been used to any great extent, exclusively in fast breeder reactors. Sodium-potassium alloys may become more commonly used. Mercury is very expensive and is toxic, as well as having too high a capture cross-section for use in thermal reactors. Lithium is similar to sodium in many respects, but has a higher melting point and is more expensive.

Sodium is the standard coolant for the still fairly small number of fast breeder reactors operating in the world. Its melting point is 98°C and its boiling point at atmospheric pressure is 890°C, so it is not necessary to use sodium at higher than atmospheric pressure, which is a distinct advantage. It is highly reactive with air and water, so high integrity pipework and heat exchangers are necessary to avoid leakage. Sodium has a fairly low capture cross-section (0.5 barns) but it does undergo the  $^{23}\text{Na}(n, \gamma)^{24}\text{Na}$  reaction, and intermediate heat exchangers are required to contain the radioactive sodium 24 within the biological shield of the reactor, as described in Chapter 7 (section 7.10). Sodium is not corrosive to most structural materials provided its oxygen content is maintained low. The formation of sodium oxide in the coolant circuit can lead to plugging unless it is removed in cold traps.

Sodium-potassium eutectic alloy with a melting point of  $-11^\circ\text{C}$  can be used for the decay heat removal systems of fast reactors as the coolant temperature in these systems may fall below the melting point of sodium.

### 10.4 Cladding materials

The fuel cladding materials require a very low neutron capture cross-section, good thermal conductivity and good strength at high temperatures to resist thermal stresses, deformation of the fuel and build up of fission product gas pressure inside the cladding. In addition the cladding should be easy to fabricate and not liable to corrosion or other chemical reactions with either the fuel or the coolant. The following metals and their alloys satisfy some if not all the above requirements, and have been considered for use as fuel cladding: aluminium, beryllium, magnesium, zirconium and stainless steel. As pointed out in section 10.2, beryllium has not proved to be a suitable

material for use in reactors, and it has not been developed as fuel cladding. Aluminium has been used as the cladding material for low power research reactors in which its temperature seldom exceeds about 100°C. Its capture cross-section is fairly low (0.23 barns) but its mechanical properties such as strength and hardness are quite low and aluminium cannot be used in situations of high stress or temperatures greater than 300°C. Consequently it cannot be used as a cladding or structural material in power reactors, and its use as noted above is solely in research reactors, in which it is often used in the form of an inter-metallic compound with uranium.

Magnesium has a very low capture cross-section (0.063 barns) but like aluminium it is a soft metal of low strength with a maximum operating temperature of about 450°C. It is also very reactive, oxidizing readily in air. The characteristics of magnesium particularly as regards oxidation, can be greatly improved by the addition of small quantities (less than 1 per cent) of aluminium and beryllium, and the alloy thus formed, called Magnox, has been used extensively as the cladding material in British gas-cooled reactors. However, the maximum operating temperature of Magnox is about 450°C, and this places a limit on the thermodynamic performance of these reactors.

Zirconium has a low capture cross-section (0.185 barns), a high melting point (1850°C), good mechanical properties and a high resistance to corrosion by water. These properties make it an excellent cladding material for reactors. The mechanical properties and corrosion resistance can be further improved by alloying zirconium with small quantities of tin (1.5 per cent), iron (0.15–0.2 per cent), chromium (0.1 per cent) and nickel (up to 0.05 per cent). The resulting alloys, Zircaloy-2 and Zircaloy-4, are used extensively as the cladding and in-core structural materials for water and heavy water moderated and cooled reactors. They are the pre-eminent fuel cladding materials at the present time.

At very high temperatures, above about 1000°C, zirconium and the Zircaloys can react with steam to form hydrogen, which is potentially very hazardous. The conditions which might give rise to this reaction can occur after a reactor loss-of-coolant accident when the fuel and cladding overheat as a result of inadequate decay heat removal. If the cladding temperature exceeds 1000°C and the cladding comes into contact with steam, then the hydrogen producing reaction occurs, possibly with explosive results.

Stainless steel is well known for its excellent mechanical properties and corrosion resistance. Unfortunately its capture cross-section, which depends on the type of steel and the precise quantities of chromium and nickel in it, is too high for stainless steel to be regarded as ideal for fuel cladding or other in-core uses. It is not now used as fuel cladding in pressurized water reactors, but it is used in the advanced gas-cooled reactor and in fast breeder reactors. In the latter the rather high capture cross-section is of less importance than in thermal reactors. Stainless steel is used extensively

for out-of-core uses in PWRs and FBRs where its excellent corrosion resistance is invaluable.

### 10.5 Control materials

Materials for controlling reactors need to have high capture cross-sections. Several such materials are available. In addition other materials of lower cross-section can be used in the reactor core for 'flux-shaping' and fine control. Stainless steel rods can be used for this purpose.

Of the control materials, boron ( $\sigma_c = 760$  barns) is the most common. It cannot be used by itself, but may be alloyed with steel or used in the form of boron carbide encased in steel. Boron can also be used to compensate for long term changes of reactivity (such as fuel burnup) in the form of a burnable poison, boric acid, dissolved in the coolant of a pressurized water reactor.

Indium and cadmium both have high capture cross-sections (195 and 2450 barns respectively) but both have melting points which are too low to permit their use in power reactors. In the form of an alloy containing 80 per cent silver, 15 per cent indium and 5 per cent cadmium, these elements are used as control rods in pressurized water reactors. The alloy has an adequately high melting point, but must be encased in stainless steel to protect it from corrosion.

Hafnium ( $\sigma_c = 113$  barns) is a good control material, having adequate mechanical strength and good corrosion resistance. However, it is too expensive to be used on a large scale for commercial reactors.

Gadolinium ( $\sigma_c = 46\,000$  barns) is used as a burnable poison in some reactors such as the advanced gas-cooled reactor.