

Technical Review

Carbon-based Materials for Atomic Energy Reactor

D. Sathiyamoorthy^{*} and A. K. Suri

Materials Processing Division, Bhabha Atomic Research Centre, Bombay-400 085, India

^{*}e-mail: dsati@magnum.barc.ernet.in

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Abstract

Carbon and carbon-based materials are used in nuclear reactors and there has recently been growing interest to develop graphite and carbon based materials for high temperature nuclear and fusion reactors. Efforts are underway to develop high density carbon materials as well as amorphous isotropic carbon for the application in thermal reactors. There has been research on coated nuclear fuel for high temperature reactor and research and development on coated fuels are now focused on fuel particles with high endurance during normal lifetime of the reactor. Since graphite as a moderator as well as structural material in high temperature reactors is one of the most favored choices, it is now felt to develop high density isotropic graphite with suitable coating for safe application of carbon based materials even in oxidizing or water vapor environment. Carbon-carbon composite materials compared to conventional graphite materials are now being looked into as the promising materials for the fusion reactor due their ability to have high thermal conductivity and high thermal shock resistance. This paper deals with the application of carbon materials on various nuclear reactors related issues and addresses the current need for focused research on novel carbon materials for future new generation nuclear reactors.

Keywords : A. Carbon/carbon composites; B. Graphite; C. Pyrolytic carbon; D. Coating; E. Chemical vapor deposition

Carbon materials possess several properties such as their capability to withstand high temperature (in protective environment) up to 2500°C, chemical inertness, low coefficient of thermal expansion, low friction, good thermal and electrical conductivities, low density, and good thermal shock resistance. Carbon based materials and graphite are widely used in nuclear applications. Graphite was used in the first nuclear reactor CP-1, constructed in 1942 at Stagg Field University of Chicago [1]. Earlier Fermi and his collaborators had assembled the first experimental graphi-teuranium structure for determining the multiplication factor (K), the ratio of number of neutrons in any one-generation to the number of corresponding neutrons in the previous generation. The first pile constructed of U₃O₈ and AGX graphite yielded K_∞ 0.944 [1]. It is difficult to fracture graphite by thermal shocks and its creep rate is very small below 1500°C. The tensile strength of graphite increases with temperature and is about twice at 2500°C as compared to that of the ordinary temperature. Graphite does not melt but sublimates at 3650°C.

Although the properties of graphite make it suitable for many nuclear applications such as moderator, reflector, fuel-channel sleeve, thermal column, fuel matrix, and control – rod material, by far its greatest use has been as a moderator and reflector. Carbon is used as moderator and reflector due to its neutron interaction characteristics, heat transfer properties, corrosion resistance, stability under irradiation, mechanical strength, low atomic weight with high neutron scattering probability, and low capture probability. Besides the lower cost and availability are the attractive features with carbon.

The main function of the moderator is to reduce the kinetic energy of the fast neutrons released at fission. Fast neutrons have energies of the order of 2 MeV, an energy level at which they are not readily captured by the fuel to sustain the fission reaction. Neutrons having thermal energies of the order of 0.025 to 0.1 eV are ideal for sustaining the fission reaction, thus it is necessary to reduce the energy of the fast neutrons. The moderation process is implemented by repeated elastic collisions of the neutrons with the nuclei of the moderator material. At each collision a neutron transfers a part of its energy to the moderator nucleus. The smaller the mass of the moderator nucleus the larger the transferred energy, which attains its maximum value when the moderator nucleus has the same mass as that of the neutron. If the energy of the recoil (knock-on) nucleus of the moderator is sufficient to permit to be displaced from its normal (equilibrium) position in the space lattice, physical changes may be observed. As a general rule, the primary knock-on atom (nucleus) acquires sufficient kinetic energy to displace another atom by collision and the latter becomes a secondary knock-on. The process will continue until the displaced atom does not have sufficient energy to eject another atom from the equilibrium position [2].

Graphite is a primary material for the construction of gas cooled reactor cores. Graphite is strong enough to serve as a structural component, this eliminates the use of metal with higher neutron absorption cross section. Theoretical density of graphite is 2270 kg/m³. However, graphite of density 1600-1700 kg/m³ are used because of the manufacturing cost. Reactor grade graphite of density up to 2000 kg/m³ has

been reported in literature.

Graphite is chosen in many reactors as moderator or reflector since it is readily available and cheaper than heavy water and beryllium/beryllium oxide. The main problem with graphite is its reaction with oxygen and with water vapour. It also reacts with metals and metal oxides and forms carbides. However, it has good thermal conductivity, which is a desired property for a moderator. In recent times, graphite with suitable coating is being developed to make it chemically inert in the oxidizing environment. Advanced gas cooled reactor (AGR), the high temperature gas-cooled reactors (HTGR), the molten salt breeder reactors (MSBR), and the liquid metal-fuelled reactors (LMFR) are all used as graphite moderators [1].

Graphite in conjunction with other materials is also used in the nuclear industry other than moderator and reflector. A good moderator should considerably bring down the energy of neutrons (i.e. from 2 Mev to 0.025) in one collision without absorbing the neutrons during the moderation. The ratio of slowing down power $\sum_s \xi$ (where \sum_s is a microscopic scattering cross section and ξ is the logarithm of the ratio of energy before and after collision of a neutron) to the absorption cross section (\sum_a) of a material is known as moderating ratio and it should be high for a good moderator. Among the solid moderators beryllium and carbon have moderating ratio, respectively, 150 and 170. For high cost and toxicity of Beryllium, it has constraint for its use in nuclear reactor. Carbon as a moderator and structural material stands for a material of favorable choice particularly for high temperature nuclear reactor. It is used as a control rod material when combined with some forms of boron or other high neutron absorbing elements [3] of high temperature stability without danger of meltdown. Graphite also serves as a stable matrix for the neutron absorber because it is able to withstand neutrons and localized alpha recoil damage, offering protection against gross shield degradation. It is also employed in design for gas-cooled reactors for graphite sleeves that support the fuel elements and also serve as channels for the coolant. In combination with components of U or Th graphite, it offers advantages as a matrix for fissile or fertile reactor fuel in thermal reactors. Here graphite serves dual purpose as a moderator and stable discharging phase of fuel. Due to its stability under irradiation and at high temperature, fuel degradation is minimized and fuel life is enhanced. Graphite also offers an exceptional heat transfer medium for heat removal and also resists thermal shock.

Gas cooled reactors have been in operation for over 40 years for production of electricity. The predominant area is the high temperature gas-cooled reactor (HTR) and it is a potential second-generation thermal reactor system in which the uranium and thorium sources of the world can be utilized for producing electricity. High temperature reactor (HTR) whether gas cooled or liquid cooled, the efficiency in converting fission energy into usable forms could be as high as 90%. In high temperature reactor, purified artificial

graphite is used to slow down the neutrons generated by fission to thermal velocities. It also serves as a structural material for the fuel element. There are two basic designs of fuel elements: the pebble bed reactor and the prismatic core [4]. In the pebble bed reactor, the core is made up of randomly packed spheres of 60 mm while the prismatic design is made up of stacked machined or pressed graphite stacks which also incorporates coolant channels and separate holes for fuel. Under fast neutron irradiation, graphite develops internal creep and anisotropy. Hence it is necessary to start with materials that are as isotropic as possible. This will also minimize the bulk dimensional changes due to the fast neutron irradiation and the onset of expansion, which would seriously affect the validity of the core design. This isotropy is achieved by selection of appropriate raw materials and by special processing.

The structural behavior of graphite is a complex function of the source materials, manufacturing process, chemical environment, temperature, and irradiation history. During neutron irradiation, graphite undergoes irradiation-induced changes, which are quite important in reactor design and operation. Such property changes in HTR reactors operating in the temperature range of 400 to 1700°C are greatly reduced but still continue to be a major factor in reactor technology. The radiation causes the displacement of carbon atoms by high-energy neutrons and recoil carbon atoms. These high-energy particles become lodged between carbon layer planes in the graphite and cause a relatively large increase in interlayer distance due to low binding energy of the layer planes. At low temperatures, the graphite expands and undergoes radiation-induced contraction which is related to the recrystallisation phenomena or the radiation induced stress annealing at high temperatures.

Whenever neutron of energy of 30 MeV impinges on carbon, 30,000 carbon atoms are released. When carbon-based materials are used in nuclear reactors, their properties are changed due to irradiation damage. Hence it is imperative to study in detail the radiation damage of the carbon materials before its use in nuclear components and the design as a whole. Graphite in particular tends to accumulate

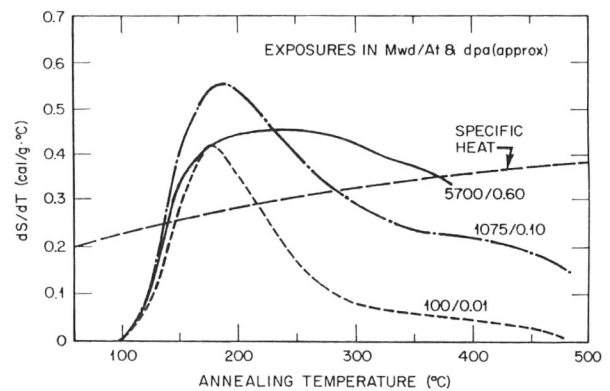


Fig. 1. Stored energy release curves of graphite irradiated at 30°C in the Handford K reactor cooled test hole [5].

or store energy due to lattice displacement, which results from knock down of carbon atoms by energetic particles such as neutrons or electrons. The stored energy is known as Wigner energy [5]. It may be noted that the binding energy of carbon atom in the graphite lattice is about 7 eV [6]. Actually on an average 30 eV is required to displace a carbon atom from its equilibrium position. The energy stored for graphite under irradiation at ambient temperature is 2720 J/g which when released adiabatically would cause its temperature to rise to 1300°C. In order to reduce or limit the stored energy it is essential to anneal the irradiated graphite. However, it is noted that stored energy ceases us to have a problem at temperature of irradiation above 300°C.

Fig. 1 shows the stored energy release curves of graphite irradiated at 30°C in the Handford K reactor cooled test hole [5]. Graphite has to be annealed frequently to remove the stored energy. If the structure is perfectly graphitic, the initial energy of the system is minimum, so it can have a lot of possibility to store energy, whereas if the structure itself is highly energetic in the beginning, the chances of more energy storage are less. This is the main reason for the carbon to be non-graphitic in nature in the state of low temperature of thermal nuclear reactors. In other words, amorphous carbon in place of graphite is an alternate choice in place of graphite. But the research on the development of irradiation studies of such materials are deficient.

A high temperature reactor contains spherical coated fuels. An individual particle consists of a kernel of fissile or fertile fuel surrounded by number of layers, which are designed to retain the fission products that are formed during the course of irradiation. The fuels may be oxides, carbides or mixed oxide/carbide forms of uranium, plutonium or thorium. Two distinct particle designs have been employed namely the BISO (Bi-isotropic) coated fuels and the TRISO (Tri-isotropic) coated fuel [4, 6]. The BISO coated particles possess two layers, a highly porous pyrocarbon (PyC) coated (buffer layer) by a denser PyC layer. BISO particles have only been employed in fertile fuel particles in low irradiation temperature and low burnups. In the TRISO coated particle, the kernel is coated by a buffer layer followed by three successive layers, such as the inner pyrocarbon (IPyC), SiC layer, and an outer pyrocarbon (OPyC) layer (Fig. 2).

The buffer PyC is designed to protect the denser IPyC

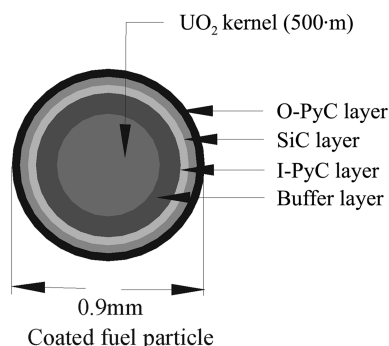


Fig. 2. A typical TRISO-coated fuel particle.

layer from damage by recoiling fission fragments emanating from the kernel and is essentially a sacrificial coating [7]. It also provides voidage for the gases that were created by fission and exerted on the outer dense PyC layer in decreasing of the pressure. The IPyC layer serves as a barrier to gross diffusion of kernel material (actinides or fission products), which may affect the inner silicon carbide layer. The IPyC layer is to protect the fuel kernel from chlorine compounds that are produced during the process of deposition of SiC layer from gas such as methyl trichlorosilane. The SiC interlayer is relatively a better diffusion barrier to metallic fission products than pyrocarbon. Its stability under fast neutron irradiation imparts dimensional stability to the whole particle. The outer PyC layer protects the SiC coating from possible mechanical interactions and chemical attacks. During irradiation, both the PyC layers shrink counteracting the hoop stresses created by the gas pressure.

There is a good amount of literature on TRISO coating of any desired property with a trial and error method. The interest in TRISO coated fuel started to recede in the late 1970's due to the less interest in HTR. Recently there has been a growing interest in commercialization of coated fuel particle with good endurance during the normal lifetime nuclear reactor. Though there is a good collection of studies on irradiation effect of carbon materials, not much is available on PyC coated fuel particle more particularly on those stress models that predict the particle failure during specific accident scenario.

There are attempts to deposit simultaneously two phase mixture of PyC and SiC over particles and such two phase mixture known as pyrocarbon alloy is believed to have superior irradiation performance as compared to TRISO coating. The details of pyrocarbon alloys can be found elsewhere in the literature [9]. Some of the interesting properties of pyrocarbon alloys are low fission product diffusion coefficient; less radiation induced dimensional changes and strong-coated layers. There is lack of extensive irradiation studies

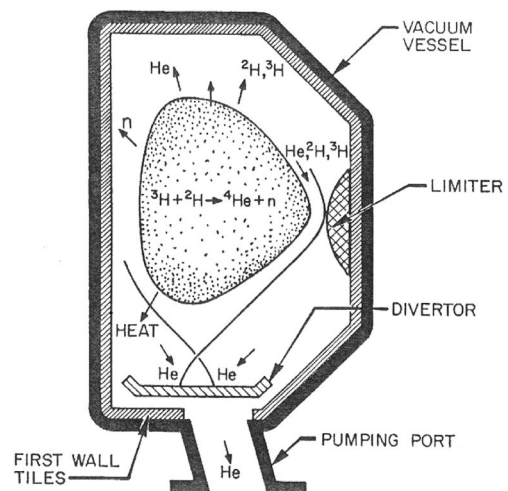


Fig. 3. Schematic diagram of the plasma-facing components (PFC) of a Tokamak fusion reactor [9].

on this alloyed particle. This alloy coating is proposed for application for BISO coated fertile particles with limited burn up. Pyrocarbon alloys for BISO particles can be reprocessed and the fuels can be separated.

More recently, Pyrolytic graphite, artificial fine grained graphite, and C-C composites have been adopted as plasma facing components in fusion devices [7]. Extensive uses of carbon-carbon composites and fine grained graphite as plasma-facing materials can be found in Tokomak Fusion Test Reactor (TFTR), Joint European Torus (JET), Tore Supra, and JT-Gouin in Japan. Tokomak fusion devices utilize carbon materials for their first-wall linings, limiter, and for armor on their plasma - facing components (PFC) as shown in Fig. 3. C-C composites possess a number of attributes such as low atomic number, high thermal shock resistance, high sublimation temperature, and high thermal conductivity, which makes it a good choice in the fusion reactors. C-C components materials may be the choice for the next generation Tokomak fusion reactors such as International Thermonuclear Experimental Reactor (ITER) which must endure severe environment including high-heat fluxes, high armor, surface temperature, and eddy-current induced stresses during plasma disruption. The plasma-facing carbon-carbon composite materials will suffer from structural and property degradation as a result of carbon atom displacements and crystal lattice damage, caused by impinging high-energy fusion neutrons and energetic helium ions for carbon transmutations. As C-C composites are infinitely variable family of materials, the processing and design variables such as; (1) architecture, i.e., 1D, 2D, 3D or random fiber distribution; (2) fiber precursor, i.e., pitch, polyacrylonitrile (PAN) or vapour grown; (3) matrix, i.e., liquid impregnation (pitch or resin) or CVI; and (4) final graphitization temperature will influence the properties and behaviour of C-C composites. Burchell et al. [9] irradiated 1D, 2D, and 3D C-C composites at 600°C and damage doses up to 1.5 dpa. 3D C-C composites were shown to have more

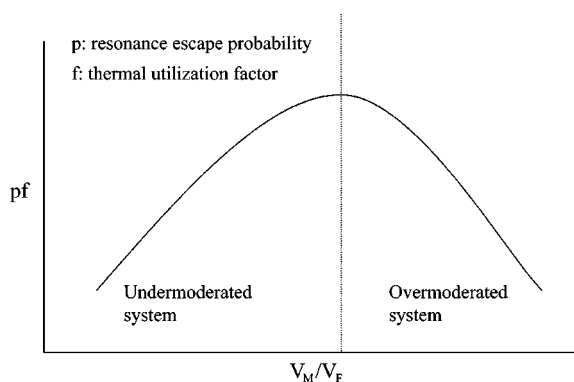


Fig. 4. Diagram showing the relation between reactivity (here represented by pf) and moderator to fuel volume ratio (V_M/V_F). In the case of an undermoderated system the reactivity comes down with decrease in V_M/V_F (i.e. creation of voidage). So under-moderated system has negative void coefficient of reactivity and it is thus inherently safe.

isotropic dimensional changes than that of 1D or 2D composites. Pitch fiber composites were shown to be more dimensionally stable than PAN fiber composites and high graphitization temperatures were found to be beneficial.

Though the use of graphite is well known in HTR as moderator/reflector, it cannot be used for the same purpose in low temperature thermal reactors. This is because of the Wigner energy which accumulated in the graphite lattice as a result of irradiation and released suddenly near a temperature around 200°C as discussed earlier. In HTR this stored energy is annealed out. In low temperature thermal reactor carbon in its amorphous form may prove to be a potential candidate in place of graphite. In an innovative design of thermal reactor in India, amorphous carbon is intended to be used as scatterer for neutrons in order to achieve negative void coefficient of reactivity through under-moderation. Negative void coefficient of reactivity refers to the situation when the reactivity in the nuclear reactor comes down with creation of voidage in moderator or coolant and this can be achieved in under-moderated system as shown in Fig. 4. The products of p (resonance escape probability) and f (thermal utilization factor) represent the reactivity. When voidage is created the ratio of moderator volume to fuel volume (i.e. V_M/V_F) decreases. It is clear from Fig. 4 that reactivity is decreased in the case of an under-moderated system.

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