

Inhibition of oxidation in nuclear graphite

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Abstract

Graphite is a fundamental material of high-temperature gas-cooled nuclear reactors, providing both structure and neutron moderation. Its high thermal conductivity, chemical inertness, thermal heat capacity, and high thermal structural stability under normal and off-normal conditions contribute to the inherent safety of these reactor designs. One of the primary safety issues for a high-temperature graphite reactor core is the possibility of rapid oxidation of the carbon structure during an off-normal design basis event where an oxidising atmosphere (air ingress) can be introduced to the hot core. Although the current Generation IV high-temperature reactor designs attempt to mitigate any damage caused by a postulated air ingress event, the use of graphite components that inhibit oxidation is a logical step to increase the safety of these reactors. Recent experimental studies of graphite containing between 5.5 and 7 wt% boron carbide (B_4C) indicate that oxidation is dramatically reduced even at prolonged exposures at temperatures up to 900°C. The proposed addition of B_4C to graphite components in the nuclear core would necessarily be enriched in B-11 isotope in order to minimise B-10 neutron absorption and graphite swelling. The enriched boron can be added to the graphite during billet fabrication. Experimental oxidation rate results and potential applications for borated graphite in nuclear reactor components will be discussed.

Introduction

Current Generation IV high-temperature gas-cooled reactors (HTR) are predominately constructed of graphite structural components and graphite fuel elements. The two basic types of HTRs are a prismatic-block or a pebble-bed design. Both design types have an annular active core region enclosed by an inner and outer graphite reflector. The annular region is composed of either prismatic fuel blocks or spherical fuel pebbles where both blocks and pebbles are primarily graphite with embedded low-enriched uranium particles (microspheres). For a nominal core power rating of 350 MW (thermal), the total mass of graphite in these proposed nuclear reactor cores can approach a massive 500 MT of graphite.

The Generation IV designs are cooled with helium gas at temperatures in the range of 550-850°C and at a pressure of 7MPa. In an off-normal event, such as a breach in the primary coolant circuit, the helium gas could escape and the containment building atmosphere could enter the hot core via the primary circuit. To mitigate oxidation damage to the graphite core, the containment building atmosphere is pure nitrogen gas (N_2). If the containment building is simultaneously breached, atmospheric oxygen may enter the containment building and the hot reactor core, then the potential for graphite oxidation exists.

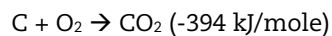
In the case of the prismatic reactor design, the fuel block is a hexagonal graphite block with vertically-drilled cylindrical holes for fuel rods and coolant channels. Under normal operating conditions, the fuel rod average can typically reach a normal operating temperature of 1250°C and heat the surrounding block graphite to 900°C. The coolant channel surface is in direct contact with the cooling helium gas and in an off-normal air

ingress event this surface would be exposed to the oxidising atmosphere. Because gaps exist between the stacked hexagonal blocks, a bypass flow of helium gas is created around and between fuel blocks. Hence, all external prismatic block surfaces could potentially be exposed to oxidising effects of the ingress atmosphere. Since the inner and outer reflector regions are also composed of stacked hexagonal blocks, the bypass flow could also contact the surfaces of these blocks. Therefore, virtually all block surfaces in the prismatic-block core design including core support pedestals could be borated in order to reduce potential of oxidation from an air ingress event.

In the case of the pebble-bed reactor design, the fuel pebbles (~6 cm diameter) are loaded into the annular core region and cooled by the helium gas flow over the pebble. The outer graphite surface of each pebble is in contact with the helium gas. Boration of the outer graphite surface of each pebble would also provide an oxidation-reduction benefit. Similarly, the graphite surfaces of the inner and outer graphite reflectors in contact with the helium gas would likewise need to be borated.

Graphite oxidation characteristics

Graphite can undergo appreciable oxidation at temperatures as low as 400°C in air. In the event of a large break of the helium coolant circulation system, oxygen would be available to convert the solid graphite to gaseous carbon monoxide (CO) and carbon dioxide (CO₂) according to the following exothermic reactions:



Heat from these reactions and the reactor core would also allow a portion of the CO₂ to convert to CO:



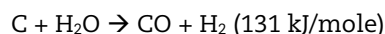
The rate of reaction and the net change in a graphite structure is dependent on the exposed graphite surface area, connected porosity, and degree of graphitisation, as well as the availability of oxygen, reaction temperature, and net absorbed radiation dose [1].

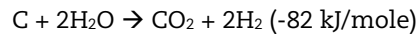
Early Atomic Energy Commission (AEC) tests indicated that irradiation led to in oxidation increases that were multiples of that seen in unirradiated material. Kosiba and Dienes [2,3] noted up to an 18-fold net increase in oxidation at 300°C for material that had previously been irradiated when it was placed in a 610 000 R/hr gamma field. The graphite in these tests was exposed to a fluence of 4×10^{20} neutrons/cm², yielding an estimated 2% atom displacement. In this case, the graphite was noted as being “low grade” material. The conclusion was that irradiation displaced atoms, which may be equated with creation of active sites that promoted more rapid oxidation.

Testing of a presumably higher grade of synthetic graphite in England [4] showed that irradiation enhanced oxidation selectively. Examination showed pitting attack at pores and grain boundaries increased by approximately one order of magnitude, as compared to unirradiated material. Pitting was observed on the 0001 face of the crystal, with pit density of 5×10^{10} /cm² to 5×10^{11} /cm². The pitting was linked to metallic impurities in the graphite. Surface characterisation was done by scanning electron microscopy, with Moire patterns indicating increased presence of interstitial atoms in the irradiated graphite. The irradiation fluence was 2×10^{19} n/cm².

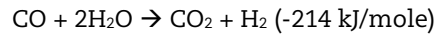
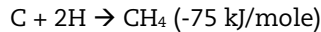
Oxidation experimentation by Davidge [5] produced results indicating that oxidation was variable and greatly dependent on oxygen flow.

Several other researchers have shown that the presence of water (as steam) dramatically increases oxidation. As seen below, the reaction with water vapor has a higher enthalpy, and hence, a much higher reaction rate.





The hydrogen may also react with the carbon to yield



For off-normal HTR air ingress events, moisture in the air could contribute to the oxidation of the reactor core graphite.

Experimental work

The ability of irradiated borated graphite to resist oxidation was observed during post-irradiation examination of graphite components from the Advanced Gas Reactor-1 (AGR-1) experiment. The test was irradiated at the Idaho National Laboratory in the Advanced Test Reactor (ATR). The borated graphite components were exposed to an intense neutron flux over a period of 3 years, or 620 effective full power days. Accumulated fast neutron fluence (>0.18 MeV) on the graphite reached $>4.0\text{E}+21$ n/cm². The boron was natural boron containing approximately 19.9 atom percent B-10. The B-10 atoms fissioned in the neutron flux creating energetic helium and lithium nuclei [$n + {}_5^{10}\text{B}_5 \rightarrow {}_2^4\text{He}_2 + {}_3^7\text{Li}_4$] which further displaced graphite atoms and lead to some amount of swelling as in graphite components.

It was in these irradiated graphite components that the degree to which boron can inhibit oxidation was observed.

The AGR-1 experiment was composed of six capsules stacked axially, numbered from 1 to 6, bottom to top as inserted vertically in the reactor. The holders in Capsules 1 and 6 contained 5.5 wt% natural boron carbide (B₄C), while holders in Capsules 2-5 contained 7 wt% B₄C. The higher boron content was reduced compact fission power in the ATR core midplane. This material was produced as a special test by GrafTech, Inc. (UCAR Carbon).

The time-averaged, volume-averaged temperature of each experiment capsule containing the irradiated borated graphite components (compact holders) was 1 200°C. The tristructural isotropic (TRISO)-particle fuel compacts placed in the graphite holders isolated the compacts from the steel capsule wall (experiment pressure boundary). The irradiated, borated graphite holders were approximately 101.6 mm (~4 inches) in length with a 50.8 mm (~2 inch) outer diameter. The total graphite holder was approximately 45 g. As fabricated, the holder approximate surface area is 28 000 mm² including the 3 vertical holes that contained the compacts. The holders were broken into pieces following removal of the compacts so that they could be transferred by pneumatic capsule (rabbit) from the disassembly cell to the analytical laboratory hot cell where the oxidation and leach processes were performed. The experiment contained 6 holders, one per experiment capsule. Efforts to oxidise the holder graphite to recover mobile fission products led to the observation that the presence of boron greatly inhibits oxidation. Oxidation temperatures ranged from 500 to 900°C in air. When it became apparent that the holders were not being decomposed effectively, a baseline test using 1 g of unirradiated, non-borated graphite was performed. That test indicated that complete ashing occurred in a 48-hour period.

The experiment cross section indicating where the graphite holder component was located is illustrated in Figure 1 below. Figure 2 shows the post irradiation condition of the holder from Capsule 5.

Part of the post-irradiation examination process involved the determination of the distribution of the mobile fission products within each capsule. The graphite holders simulate the graphite in the fuel blocks in the prismatic design. The graphite tends to adsorb a significant fraction of most fission products released from the compacts. The gamma-emitting fission product nuclides are readily measured by gamma spectrometry,

but the beta emitters, in particular strontium-90, can only be detected by reducing the graphite to ash, leaching the ash and doing strontium separation and counting using gas proportional or liquid scintillation detection.

Figure 1: Radial cross section view of AGR-1 experiment

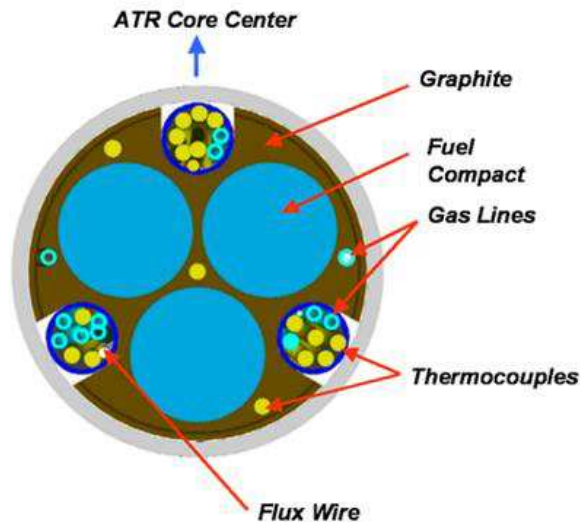
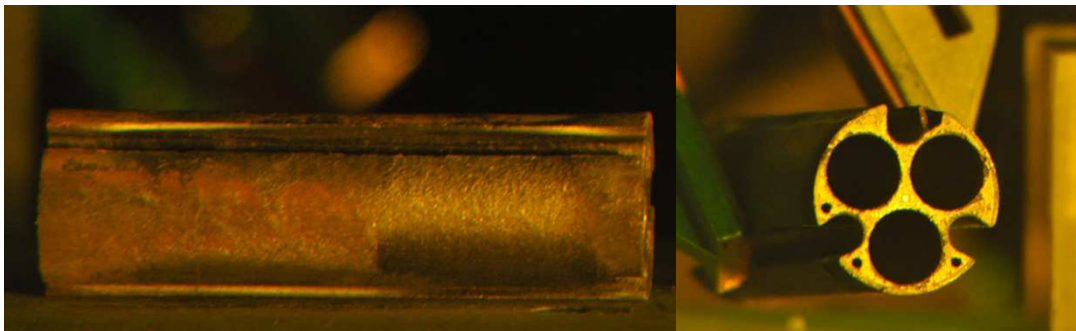


Figure 2: Graphite holder [Capsule 5 post irradiation]



Oxidation test procedure

The holders were transferred pneumatically from the hot fuel examination facility main hot cell, which is an argon atmosphere cell to the MFC-752 Analytical Laboratory air atmosphere hot cells, where wet chemistry analysis preparation can be performed. The process of oxidation and leaching was performed in Hot Cell 5, which is equipped with laboratory glassware for leaching and an air furnace for oxidation. The oxidation and leach activities were performed in shielded cells due to the relatively high activity from fission and activation products in the graphite. The process of direct oxidation was initially undertaken without recognition that the presence of boron in the graphite would affect the oxidation rate. The broken holder pieces were placed in covered (not air-tight) 150 ml quartz beakers. The beakers were placed in a Vulcan muffle furnace, which had been modified with a small fan to promote air circulation through the heated volume. Oxidation was expected to be completed in a matter of hours. Based on previous testing of several nuclear grade graphites, oxidation of greater than 15% of the mass of historical grade H-451 graphite occurred in less than 2 hours at 750°C [6].

The oxidation procedural sequence for the first AGR-1 graphite holder tested (from Capsule 3, the third from the bottom) was as follows: 168 hours at 500°C, reported as

approximately 50% volume reduction by inspection; 40 hours at 750°C with between 10 and 20% change, followed by two cycles at 900°C for 88 hours. These oxidation times far exceeded the expected time for complete conversion. Mass loss was not quantified, because the primary interest was the Sr activity measured in the dissolved ash residue. The final 3 elevated temperature cycles resulted in apparent reaction of the graphite with the silica in the beakers. The boron content in this component was 7%.

Multiple efforts were made on the second oxidation test (Holder 5) to increase availability of oxygen to ensure complete conversion of graphite to ash. This test likewise yielded incomplete ashing. The initial temperature was 750°C, which was maintained for 136 hours, and resulted in a nominal volume reduction of approximately 40% (again by inspection only). The furnace auxiliary blower was set to produce a minimal flow. Following the burn phase the exposed surfaces of the pieces in the beaker were generally white. The second burn continued for 15 hours at 750°C and 24 hours at 900°C. The sample appeared to have melted and one of the two beakers containing the graphite showed some cracking. The third burn was performed at 900°C for 96 hours. By inspection, the graphite in the two beakers was reduced to approximately 15% and 6% of the original volume, respectively. The slow rate of decomposition led to the conclusion that the material did not have sufficient oxygen supply during heating for complete oxidation. Reconfiguration of the beaker lid to allow more airflow and increasing the power to the furnace blower were tried in an effort to improve oxidation rate. The fourth burn was performed for 55 hours at 900°C with the furnace fan at 80% of maximum voltage and the beaker covers removed. The residue at the end of the burn was largely unchanged from previous burn steps. The process is illustrated in Figures 3 through 6 below.

Figure 3 shows two beakers in the furnace containing gray-black and whitish vertical, free-standing pieces that largely retain their initial shape. Figure 4 shows that the material is still able to maintain a vertical shape, while Figure 5 shows the eventual reduction in height and in Figure 6, the attack on the fused silica beaker is visible.

On the assumption that there was a mass transport limitation, the third and fourth holders tested were ground to a nominal 1 mm diameter using a rotary manual grinder. This resulted in minimal change in conversion effectiveness. The particulate agglomerated somewhat, with minimal volume reduction.

Figure 3: Graphite holder pieces following first burn step (136 hrs @ 750°C)



**Figure 4: Graphite holder pieces following second burn step
(15 hours @ 750°C and 24 hrs @ 900°C)**



Figure 5: Graphite holder pieces following third burn step (96 hrs @ 900°C)



The observed condition after the first two oxidation steps was an apparent glassy surface. Further review of the holder chemistry raised the issue of boron content. A conclusion was reached that the boron-10 was being converted to lithium as a result of neutron irradiation, forming an impermeable glassy lithium carbide surface. Because lithium carbide is water soluble (reacting to form acetylene gas and lithium hydroxide), a process of alternately leaching the material with demineralised water or nitric acid followed by an oxidation cycle. Because it did not generate a gas bubbling reaction, it was concluded that the surface was not Li_4C_2 . The material was impervious to insoluble in 4 M HNO_3 . It was light and floated on the surface. From these characteristics, it is postulated that LiOH

(MP 450°C) or Li_2CO_3 (MP 723°C) were formed which reacted with the quartz beaker, leaving behind an insoluble borosilicate material. Because the boron used in the holder graphite was natural abundance, only 20% was B-10, meaning that even though the accessible lithium carbide may have dissolved, the remainder was still present as boron-11.

Figure 6: Graphite holder pieces following fourth burn step (55 hrs @ 900°C)



From the discussion of the processes applied, it was apparent that the graphite material was not completely converted to CO or CO_2 . To confirm that the system was not oxygen limited, a comparable non-borated graphite sample placed in the same hot-cell furnace was reduced to ash in 8 hours at 750°C. The image following the first burn indicates that the material still has enough structural integrity to remain in its general original upright configuration. Compression testing is required to determine the degree to which boron-containing graphite retains the desired properties following oxidation.

A final technique using sodium-potassium alkali fusion on small samples of the borated holder graphite ground to flour consistency made no definitive improvement on the degree to which the graphite was converted to gas, and the recovery of residual strontium. In this test, the chunks of graphite were ground to a powder using a lab grinder, and 1 g samples were mixed with 6 parts of equimolar $\text{Na}_2\text{K}_2(\text{CO}_3)$ and fused in the furnace at 750°C for 2 hours in a zirconium crucible. The fused salts were dissolved in 8 M nitric acid. The intent was to react the boron carbide with the carbonate salts and separate them from the remaining graphite. The residue was then returned to the furnace for 8 hours, ramping up from 650 to 725°C followed by leaching with nitric acid. Analysis was performed on both the fusion and post-burn leach solutions. Testing on unirradiated material showed effective conversion, with greater than 80% of the graphite being consumed. For the irradiated material, the mass-normalised strontium analysis results were not significantly greater than by the other methods. Gamma ray activity on the resultant filtrate indicated that not all of the graphite was converted to CO or CO_2 .

Other examples of oxidation inhibition due to boron in graphite

Since at least 1984, work has been published indicating the oxidation inhibition effects of boron in carbon materials. McKee [7] found that carbon-composites sealed with borate resisted oxidation at 1 200°C. Boron-doped graphite fibre has been tested for oxidation resistance in aerospace applications where the fibre must perform under high temperature conditions at leading edges of airfoils. Howe [8] tested fibres with 3.3 and 4.6% boron and suggests that 1% is the minimum at which oxidation is affected.

Although the borated graphite used in the AGR experiment was prepared as B_4C , similar changes in oxidation inhibition were seen in graphite impregnated with B_2O_3 . Savchenko [9] observed a 150°C increase in the oxidation temperature of borated graphite foil. Approximately 2 wt% boron oxide was incorporated into the graphite. Physical properties of flexibility and tensile strength were also enhanced by the inclusion of boron oxide. It is also noted that it is less effective if it is applied as a surface coating rather than impregnating the boron into the graphite.

In some instances, boron acts as a catalyst with regard to oxidation, but it generally inhibits oxidation when present in concentrations beyond a certain percentage. At approximately 4% boron in Saran char, Karra [10] reported an approximate 50% inhibition, while 1.1% boron concentration resulted in a nominal 75% increase in oxidation. Multiple explanations have been offered to explain the inhibition, including boron's effect on increasing graphitisation, as well as the substitution of boron into the graphene structure in place of carbon.

The fact that boron inhibits oxidation in carbon materials has been established. Inclusion of boron in materials for nuclear service has not been widely studied, because of boron's neutronic effects. Because the fuel density of the high temperature reactor is quite low, and the potential neutron absorption by boron, the concerns about neutron economy have generally been presumed to outweigh the positive oxidation effect of boron on carbon. However, natural boron is approximately 20% B-10, which has a thermal neutron absorption cross-section of approximately 0.9 barns (0.0253 eV). The corresponding thermal neutron absorption cross-section for B-11 is 0.0055 barns. Since the B-10 absorption cross section is effectively 164 times greater than B-11, it will be necessary to use boron enriched in the low-absorbing B-11 isotope for application in an HTR for graphite oxidation inhibition. Adding B-11 to block or pebble graphite in an HTR will supplant some carbon atoms, however, the substitution of carbon atoms with B-11 atoms will not create a neutronic reactivity impact to the active core, since the carbon thermal absorption cross section is very small and almost the same as the B-11 cross section. Likewise, the neutron scattering cross section for B-11 is almost identical to that of C-12, which is the main constituent of graphite, hence damage due scattering is expected to be equivalent.

Conclusion

The oxidation tests reported here indicate that presence of 5.5 to 7 wt% boron carbide in graphite inhibits oxidation, even though the neutron capture by boron-10 created more active sites for oxidation reaction. For application to high-temperature gas-cooled reactors, graphite fuel, reflector and support structures could be borated with B_4C enriched in boron-11. Based on our experiments, this inclusion could significantly reduce graphite oxidation (corrosion) during a postulated air ingress event.

Additional tests are required to generate definitive oxidation rate and critical condition values, as well as to determine the changes in structural properties as the oxidation progresses. Compressive strength is a primary structural property of concern. Further testing is needed to determine the effect of inclusion of boron on net compressive strength.

Acknowledgements

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