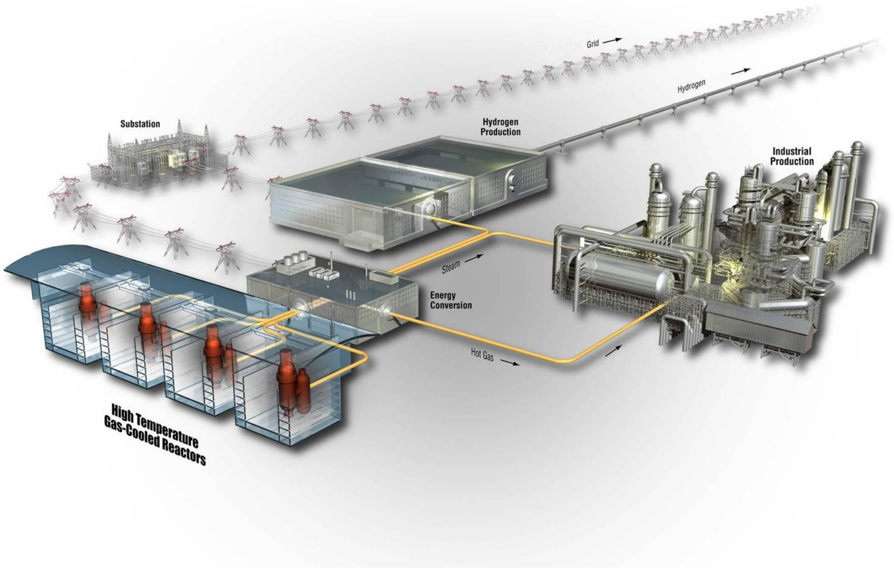
INL/EXT-14-32513
Revision 0

Oxidation-Resistant Graphite Studies

W. Windes and R. Smith

July 2014



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Laboratory

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http://www.inl.gov

Prepared for the
U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

Very High-Temperature Reactor Program

Oxidation-Resistant Graphite Studies

INL/EXT-14-32513
Revision 0

July 2014

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7/15/14
Date

ABSTRACT

The Very High-Temperature Reactor Graphite Research and Development Program is investigating doped nuclear graphite grades that exhibit oxidation resistance. In the unlikely event of an oxygen ingress accident, graphite components within the VHTR core region are anticipated to oxidize so long as the oxygen continues to enter the hot core region. For the most serious air-ingress accident which persists over several hours or days the continued oxidation can result in significant structural damage to the core. Reducing the oxidation rate of the graphite core material during any air-ingress accident would mitigate the structural effects and keep the core intact. Oxidation testing of graphite doped with oxide forming material is being conducted to determine the extent of reduction of the oxidation rate. Nuclear-grade graphite doped with varying levels of boron-carbide (B_4C) was oxidized in air at a nominal 740°C. The oxidation rates of the boronated and unboronated graphite grade were compared. With increasing B_4C content (up to 6 vol%), the time necessary to oxidize the boronated graphite was increased by 20 times what was necessary for unboronated graphite (i.e. the boronated graphite was observed to react at one twentieth the rate of the unboronated). Visual inspection and dimensional measurements were conducted to assess the uniformity of oxidation across the surface of the specimens. Future work is planned to determine the remaining mechanical strength of theses samples. Potential use of graphite grades with silicone carbide-doped material are also discussed in this report.

CONTENTS

FIGURES

TABLES

ACRONYMS

B_4C	boron-carbide
RSA	reactive surface area
SiC	silicon-carbide
VHTR	Very High-Temperature Reactor

Oxidation-Resistant Graphite Studies

1. BACKGROUND

The Very High-Temperature Reactor (VHTR) Graphite Research and Development Program is currently studying nuclear graphite doped with material promoting oxidation resistance when exposed to an oxidizing environment. Graphite core component temperatures of 1000 to 1100°C are expected under normal operating conditions and can exceed 1500°C under some accident conditions. At these high temperatures, oxygen ingress which allows significant levels of water or air into the graphite core region would result in oxidation of the graphite core components. The concern is that continued corrosion of the components resulting from an uninterrupted ingress of oxygen may compromise the structural integrity of the graphite core during a long air-ingress accident. Reducing the oxidation rate of the graphite core material would minimize the structural effects and keep the core intact during any air-ingress accident.

Previous graphite work on graphite and carbonaceous materials has been conducted by the National Aeronautics and Space Administration and the aerospace industry. These studies demonstrated that some oxygen sensitive (oxide forming) dopants added to the pre-cursor mix of engineered graphite grades can significantly reduce the oxidation rate of the graphite components.[1,2,3] The dopant additions to the graphite form oxide films that shield the bulk graphite from the available oxygen, resulting in a significant reduction in the oxidation rate. Oxide forming additives can be bonded to the surface of the finished graphite component through mechanical deposition (dipping, particle spray, etc.) but it has been shown that these interstitial bonded surface chemical inhibitors can decompose over time at high temperatures (> 400-500˚C).[4] Current practices induce an oxide layer from oxygen sensitive atoms added to the crystal structure of the graphite through a high-temperature annealing process that substitutes the metal impurity for a carbon atom within the graphene plane. These substitutional metal impurities at the graphene edge locations bond with oxygen atoms during oxygen adsorption to form a stable oxide coating.

A thermally stable oxide film acts to poison (i.e., cover/shield) the reactive surface area (RSA) within the graphite, reduces the rate of graphite oxidation by retarding the rate limiting elementary process within the quickest pathway of the reaction mechanism (i.e. the oxide barrier limits diffusion of oxygen to the RSA sites).[5,6] Coverage of the oxide film is dependent on the metal impurity level. While it is impossible to completely cover all RSA sites to halt oxidation, the introduction of these locally adherent oxide films can significantly suppress the overall oxidation of the bulk graphite material.

Several oxide-forming impurities capable of substitutional bonding within graphite are used for oxide film formation, with boron, silicon, and phosphorus being the most common. These form thermally stable oxide films, ranging from 450°C for boron dopants to as high as 1100°C for silicon. An interesting observation for the lower-temperature coatings (such as boron oxide or boro-oxy-carbides) is that they provide significant RSA poisoning well above the thermal stability of the formed oxide. This increased thermal stability is speculated to derive from an oxy-carbide forming within the pores of graphite. At temperatures higher than 450°C, the atmosphere above these oxy-carbide filled pores will tend to form a high vapor pressure, effectively stabilizing the protective film to temperatures as high as 1000 to 1100°C. Silicon based oxy-carbides also display this behavior and can be expected to survive to temperatures as high as 1800˚C.

Boron-carbide (B_4C) addition is the most common impurity added to graphite to mitigate oxidation. Normally, the boron content in nuclear reactor core components is severely limited due to ^{10}B-neutron interactions imposing a neutron penalty within the core. It has been proposed that the isotope ^{11}B with a significantly lower thermal neutron absorption cross section (^{10}B = 7000Barns, ^{11}B = 0.01Barns) could be used without invoking a significant neutron penalty instead of boron contaminated with high absorption cross-section ^{10}B. There is no indication that these material additions have ever been considered as oxidation-resistant graphite components for nuclear applications.[7] This new concept was discovered during high-temperature reactor fuel matrix material irradiation studies, a carbonaceous composite of phenolic resins and graphite particles. B_4C additive in the graphite specimen holder was employed to control the thermal neutron spectrum during fuel irradiation studies. After irradiation, the holders were to be oxidized at high temperature and any fission products retained within the graphite were to be recovered in the reaction off-gas. This proved to be difficult because the graphite did not readily oxidize, even at 750°C for 136 hours (Figure 1).[8]

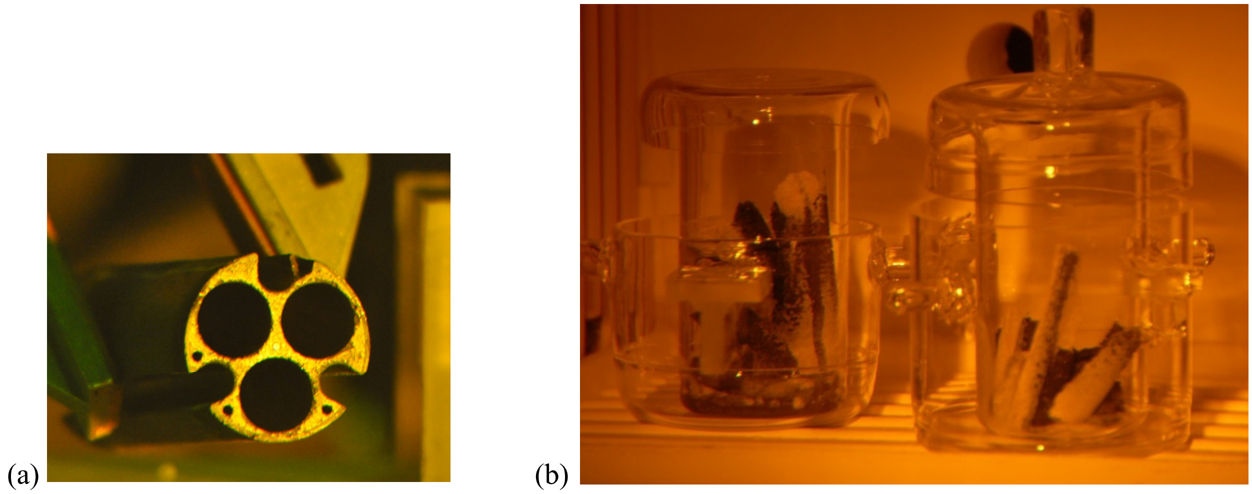

Figure 1. (a) Boron-carbide-doped fuel compact holder and (b) remaining graphite pieces after 136 hours at 750°C.

Once it was recognized that decreased oxidation resulted from the B_4C addition to the graphite, this phenomenon was investigated for further nuclear applications. A small scoping study investigating the possibility of utilizing oxidation-resistant dopants was undertaken, specifically to investigate the viability of using B_4C additions. Oxidation testing of graphite doped with B_4C material was conducted to determine the extent of reduction of the oxidation rate. Nuclear-grade graphite doped with varying levels of B_4C used previously for the Advanced Gas Reactor Fuel Testing Program was oxidized in air and compared to similar material without B_4C and other nuclear graphite grades. With increasing B_4C content (up to 6 vol%), the time necessary to oxidize the boronated graphite was increased by 20 times what was necessary for unboronated graphite (i.e. boronated graphite was observed to react at one twentieth the rate of the unboronated graphite). These results and future oxidation studies planned for lower B_4C dopant levels, as well as utilizing SiC, are discussed in this report.

2. BORON-CARBIDE OXIDATION

Because the graphite research and development program had graphite with varying contents of B_4C available, a small scoping study was conducted to determine the potential advantage of these oxide-forming additives. A small number of specimens were machined from the available material and tested within the existing oxidation testing equipment. The intent was to duplicate oxidation testing from previous studies of nuclear-grade graphite to provide a direct comparison of the oxidation rates for boronated and unboronated graphite grades.

2.1 Experimental Design

A small scoping study was designed for this new oxidation work. Similar to previous VHTR studies on nuclear-grade graphite, oxidation testing was conducted in a vertical oxidation furnace as described in detail in ASTM 7542 and previous VHTR reports (Figure 2).[9] Specimen size, oxidation temperature, and oxidizing environment were duplicated from previous oxidation studies on unboronated graphite to provide a direct comparison of the oxidation rate. Similar to previous VHTR oxidation studies, testing was performed under isothermal oxidation conditions at 740°C with 10 L per minute gas flow. The system is configured to automate gas flow and provide cooling in inert gas to facilitate recovery of oxidized samples. Mass loss during oxidation was measured after the isothermal oxidizing environment had been established in the vertical furnace. All specimens were tested to a 10% mass loss to assist in comparison of overall bulk oxidation behavior.

Figure 2. Vertical oxidation furnace as specified in American Society for Testing and Materials,7542.

A limited specimen test matrix was developed for this small study based on the available boronated graphite material. All specimen dimensions were similar to dimensions from previous studies (i.e. 25.4-mm diameter by 50.8-mm in length) to provide direct comparison of the oxidation rates for boronated and unboronated graphite grades (Figure 3). The basic specimen test matrix is shown in Table 1.

Figure 3. Specimen dimensions of 25.4-mm diameter by 50.8-mm long (specimen dimensions used in previous studies).

Table 1. Boronated graphite oxidation specimen test matrix.

Boron Content (%)	Total Specimens	Unoxidized Specimens	Oxidized Specimens
0	20	15	9
3.62	5	2	3
4.93	7	3	4
5.90	4	2	2

2.2 Oxidation Rates of Boron-Carbide-Doped Nuclear Graphite

In general, unboronated graphite grades reach a 10% mass loss within 3 hours at 740°C in 100% air (Figure 4). The addition of boron to the graphite matrix results in dramatic reductions to the oxidation rate when compared to the unboronated graphite grades (Figure 5). The oxidation rate decreases rapidly as the boron content is increased, with the 6% B_4C doped graphite observed to react at one twentieth the rate of the unboronated rate.

The rate of oxidation is reduced dramatically after the first 2 to 3 hours, when the oxide film is established (as indicted by the yellow markers on the plot). This change in oxidation rate is characteristic of these substitutional impurities that form oxide films on the graphite. It takes time and exposure to enough oxygen to form the adherent oxide film, but once it is established, the RSA poisoning leads to significant rate reduction. Lower boron content provides less RSA poisoning and, thus, less reduction in the oxidation rate.

As discussed previously, the formed oxide film does not completely halt oxidation of the graphite; the rate is just reduced dramatically. This resulted from lack of a contiguous film formed for these relatively low boron-content graphite grades. One observation from previous work of oxidizing the Advanced Gas Reactor fuel graphite holders was that the film appeared to grow more substantial and the oxidation rate continued to slow as oxidation progressed. As the carbon material at the available RSA sites is reacted and removed, more metal impurity sites are exposed, which will tend to increase the oxide film.

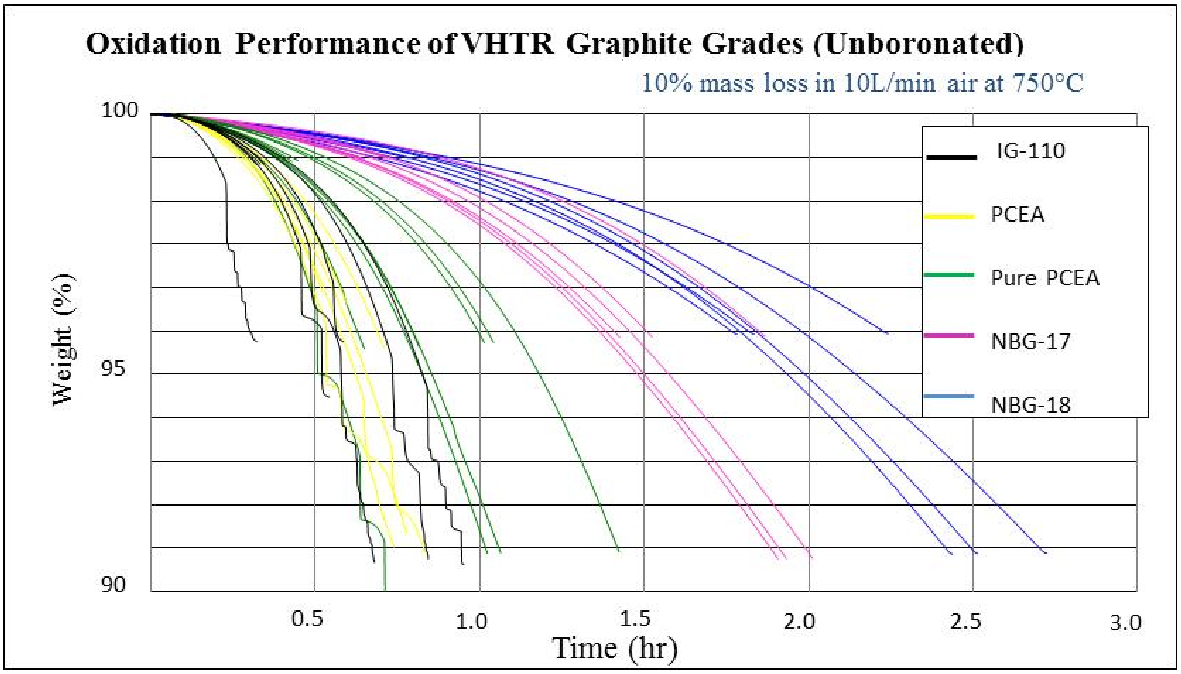

Figure 4. Oxidation performance of Very High-Temperature Reactor graphite grades from previous studies (unboronated).

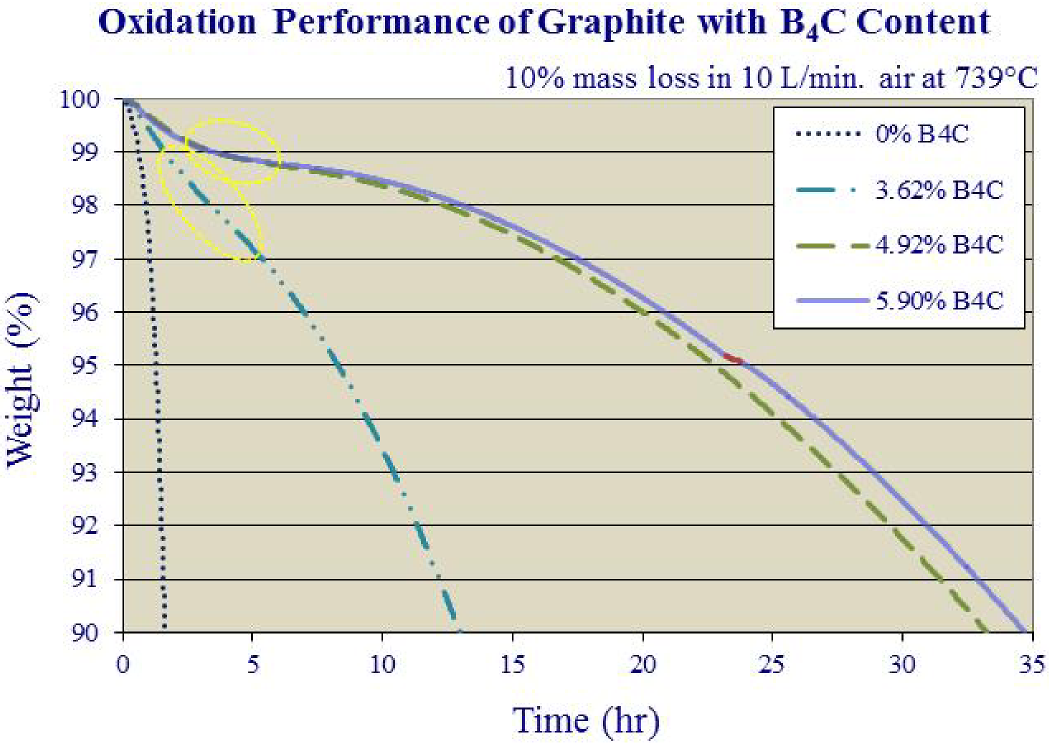

Figure 5. Oxidation performance of boronated graphite.

2.3 Discussion of Boron-Carbide Oxidation Results

Significant reduction in oxidation rates for graphite is achieved by doping graphite with metallic impurities, which can form oxide films that effectively poison reactions at RSA locations. Boronated graphite oxidation rate was one twentieth the rate of the unboronated graphite, with qualitative results indicating that the overall oxidation rate will continue to decrease as the graphite is oxidized further. It is assumed that as the carbon reacts, more boron is available to react with oxygen which increases the protective oxide film. Initial results indicate that this decrease in oxidation will assist in all accident conditions, including beyond design basis accident events, where air ingress is not impeded and a chimney effect is achieved.

However, adding B_4C to the graphite microstructure has definite limitations and some adverse effects that preclude an immediate change to nuclear-grade graphite. Issues with fabrication, additive consistency, machining, and irradiation performance must be considered before a viable nuclear application can be determined.

2.3.1 Additive Distribution within the Graphite Microstructure

Boron is a powerful sintering aid during the fabrication of graphite. Similar to boron as a micro-hardener in steels, even low levels of boron can significantly change the microstructure formation of graphite during fabrication. This can result in dramatic changes to the material properties of the formed graphite. Most graphite vendors are more than reluctant to work with boron or B_4C, because it contaminates the forming equipment and can volatilize during graphitization, distributing boron throughout the fabrication facility.

During discussions with VHTR graphite vendors concerning use of B_4C dopants for new nuclear components, there was a distinct lack of interest due to the problems of boron contamination. Contamination problems can be resolved through a separate fabrication line, thus eliminating the spread of contamination to other graphite grades. However, this is an expensive and time-consuming solution and will only occur if there is a major market for such a product.

Another issue involves the consistency of the graphite product. The B_4C-doped graphite was fabricated within a small, development process line that is used for prototype-grade materials. Perfect uniform mixing and distribution of the dopant is difficult to achieve, because the process utilizes dry components (i.e., coke filler particles with a range of particle sizes). This issue was apparent during the oxidation studies, when some specimens exhibited significantly greater oxidation rates than were measured for specimens with similar B_4C content but were derived from different fabrication batches (Figure 6). During the post-testing inspection, the visible film at the surface of the specimens oxidizing at the higher rates was not as uniform as the specimens with slower oxidation rates (Figure 7).

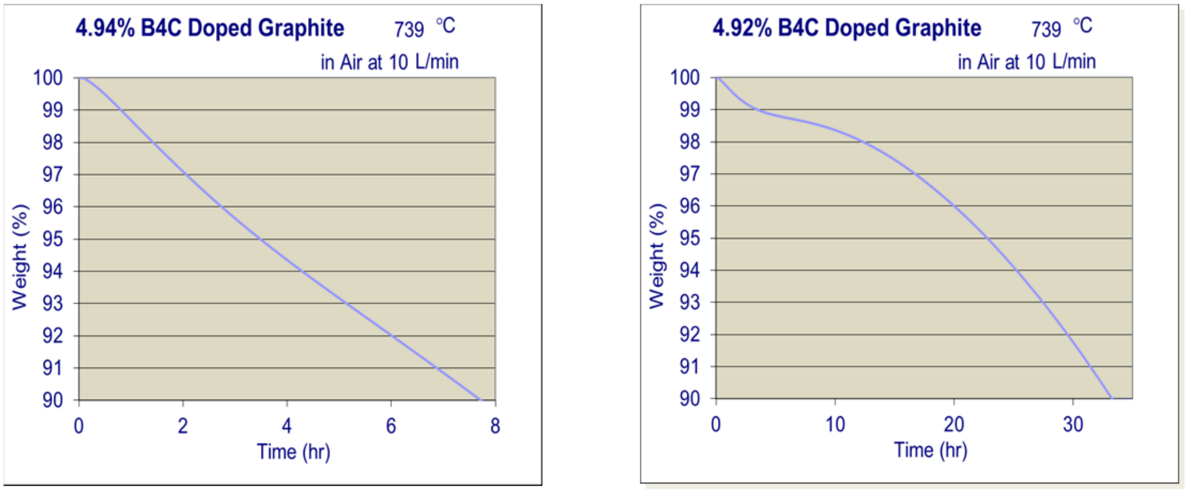

Figure 6. Oxidation rates of specimens from similar boron-carbide content, but from different billets.

Figure 7. Visual inspection of a post-oxidized boron-carbide specimen, illustrating non-uniform oxide film development on some graphite specimens.

Issues of contamination, dopant distribution, and consistency of product are fabrication issues that can be easily resolved in the future if this graphite becomes a viable and desirable grade for graphite core components. However, there must be significant demand, or the promise of a future significant demand, before the graphite vendors will be interested in developing this grade to nuclear quality levels.

2.3.2 Machining Considerations for Boron-Doped Graphite

During specimen preparation before oxidation testing, it was noted that the doped graphite did not machine as easily as un-doped graphite. In addition, it was noted that as the B_4C content increased, specimen machining became more difficult. The machining tools became dull much faster, impeding the machining efficiency and creating problems with meeting small tolerances on the specimens. It was assumed that the B_4C structure within the graphite produced very hard areas within the microstructure that dulled the cutting tools prematurely.

If core components are to be made from B_4C-doped graphite, then machining difficulties must be taken into consideration. Because the B_4C normally creates very hard structures, machining of complex components will be challenging if doped graphite components are adopted for nuclear applications. Reducing the boron content will significantly relieve the machining issues because there will be less locally hard volumes within the microstructure. Even though oxidation resistance will be minimized, there may be a compromise level of dopant that can provide enough oxidation resistance but allow complex graphite components to be machined.

2.3.3 Radiation Performance of Boron-Doped Graphite

Previous studies have indicated that in order to stabilize boron within the graphite microstructure, the boron atoms must be substituted for carbon atoms within the graphite crystal structure. This atomic substitution creates tremendous stresses within the crystal lattice structure, because boron bonds are distinctly different from carbon. This increase in crystal lattice stress can enhance damage within the graphite microstructure of a core component during irradiation.

During neutron irradiation, the atoms within the crystal structure are physically removed from their crystal lattice positions. During this ballistic event, the energy of the incoming particle (i.e., neutron or primary knock-on atom) and the energy necessary to remove an atom from its crystal lattice position (i.e., the displacement energy) dictates how many atoms are removed from their positions. Displacement energy is dependent on the bond strengths of the individual atoms and the crystal structure formation. Lower-energy bonding results in more damage from incoming particles with the same energy.

Boron-carbon atomic bond energies are different from a carbon-carbon bond found within a graphite structure. As noted, this creates large internal stresses within the crystal structure, which tend to lower the energy necessary to displace the atoms from their atomic lattice positions. The increased internal stresses resulting from boron substitution within the graphite crystal structure tends to create larger irradiation damage areas within the graphite microstructure.[10] Thus, boron tends to increase the damage rate of graphite material during neutron irradiation.

While there will be some acceleration of the irradiation changes, the long-term effect of boron additions on the overall graphite performance are relatively unknown. This is because, while the damage is accelerated, most of the graphite material property changes have reached saturation after only a few months within a nuclear reactor. Some of the long-term material properties (such as irradiation creep) may be significant enough that the long-term performance of the graphite components may be adversely affected.

This enhanced, long-term degradation may preclude boron-doped graphite components for long-term use within high-dose regions of the core. B_4C-doped graphite may be restricted to either short-term components (e.g., graphite fuel blocks) or long-term components outside the core central region (i.e., support columns and permanent reflector blocks). Similar to the machining issues, irradiation damage acceleration can be reduced by decreasing levels of boron content within the graphite components. This means using graphite material with enough boron content to provide some oxidation protection, yet not enough to significantly accelerate irradiation.

3. SILICON CARBIDE AND OTHER OXIDATION-RESISTANT DOPANTS

Other dopants (such as silicon, phosphorous, and aluminum) can provide oxidation resistance to graphite similar to boron. Silicon in the form of an silicon-carbide (SiC) additive can provide oxide films that are more thermally stable than B_4C. The protection provided by these other dopants is generally less effective than boron, but they may be sufficient for the purposes of nuclear applications. When considering other dopants for graphite oxidation resistance, the same material issues must be addressed, including microstructure changes, activation, film stability, and irradiation performance.

Aluminum and phosphorous both form oxy-carbide films; however, the adherence and thermal stability of the films is fairly low. In addition, potential activation of aluminum and phosphorous increases the radiation levels of the graphite, creating waste issues after use in a nuclear application. Aluminum and phosphorous will increase the lattice stresses beyond the boron additions, but they do not have the same reputation for creating very hard volumes inside the microstructure, which complicates machining of boron-doped graphite. While they will provide better machinability than B_4C-doped graphite, neither dopant provides a superior reason for replacing boron at this time.

SiC theoretically creates a more stable oxide film (e.g., SiO or Si-C-O) than boron. The activation of silicon is minimal and the neutron capture cross section is much smaller than ^{10}B (but slightly higher than ^{11}B). The crystal lattice stresses formed from substitutional processes are likely to be slightly higher than boron, and locally hard volumes within the microstructure will be present, but will not be nearly as hard as the B_4C-generated graphite. As such, SiC additions to a graphite grade seem to be a viable variation on B_4C in order to produce a more thermally stable oxide film that is capable of withstanding very high accident conditions. Future work with silicon-doped graphite is anticipated.

4. CONCLUSIONS AND FUTURE WORK FOR OXIDATION-RESISTANT GRAPHITE

Doping nuclear-grade graphite with boron significantly reduces the oxidation rates for graphite at relatively high temperatures and high oxygen levels. Boronated graphite was observed to react at one twentieth the rate of the unboronated achieved for the first 10% loss of mass, with qualitative results indicating that the rate will continue to decrease as the surface area of the graphite component continues to decrease. Initial results indicate that this decrease in graphite oxidation can significantly reduce core degradation during high-temperature accidents. Mechanical testing will be conducted in the future to determine the remaining mechanical strength of these oxidized specimens to ensure core stability during an oxidation event.

The outer surfaces of all doped specimens appeared to be continuous and adherent with no indications of spallation or crack formation. Based on previous work, oxide formation poisons the RSA sites, thus decreasing the opportunity for oxygen to react with carbon atoms along the graphene edge sites. The oxide forms inside the pore structure, which provides a microenvironment for increasing the thermal stability of the oxide film well above the temperature where it would normally decompose.

However, B_4C in the graphite microstructure has definite limitations and some adverse effects that preclude an immediate change to nuclear-grade graphite. Issues with fabrication, additive consistency, machining, and irradiation performance must be considered before a viable nuclear application can be determined. Large additions of B_4C can complicate the machinability of the graphite components, while also accelerating the long-term irradiation induced changes in the graphite material properties. Thus, rather than using doped graphite for all components within a VHTR core, an analysis of which components could benefit the most from oxidation resistance while minimizing the detrimental effects from oxide forming additives. Long term degradation issues can be minimized by restricting doped graphite to either short-duration components (such as graphite fuel blocks) or long-term components outside the core central region with low anticipated lifetime dose levels (e.g., support columns or permanent reflector blocks). Reducing the level of boron content within a graphite material will also relieve many of the issues surrounding machinability and irradiation performance. While the graphite oxidation rate will increase at lower additive content, an optimal dopant level can be determined which will provide acceptable performance for short-term oxidation protection as well as long-term irradiation stability and machinability for VHTR core components.

Finally, while B_4C provides excellent oxidation protection for graphite to high temperatures, the oxide will eventually start to degrade at temperatures approaching 1000 to 1100°C, depending on the pore structure on the graphite surface. Using SiC as an additive may provide a more thermally stable oxide film that can provide oxidation protection at the highest anticipated accident temperatures (1600 to 1800°C). While not as efficient in producing an oxide film as boron, an Si-O or Si-O-C film may poison the RSA locations sufficiently to reduce overall oxidation rate enough to ensure core stability for even the most aggressive oxidation ingress events (e.g., beyond design basis accident).

Future work will address the mechanical strength of the oxidized specimens to determine the remaining strength. Following these successful oxidation tests of doped material, the possibility of applying surface coatings of dopant after machining will be tested. The intent is to provide oxidation resistance to only the areas that are exposed during an air ingress accident event (which is the outer surface of the graphite components) while minimizing or eliminating the issues that occur from adding dopants to the entire graphite material (e.g., machinability issues or irradiation performance degradation).

Surface application processes utilizing B_4C and SiC powders will be tried to provide a light coating to the outer surface of the machined unboronated graphite specimens. The coating is not required to provide complete coverage, because all that is needed is a reduction in the oxidation rate, not elimination of oxidation. Various thermal processes to provide limited substitution on the outer surface of the graphite components will then be investigated. These surface-modified graphite specimens will be oxidized and mechanically tested to determine the viability of the oxide coatings.

5. REFERENCES

[1] P. A. Thrower, “Chemistry and Physics of Carbon – A series of advanced”, Volume 23, *Marcel Dekker, Inc.*, 1965.

[2] Q. Wang, et al., “Effect of boron on graphite oxidation – a theoretical study”, Carbon 35 [2], pp 307-313, 1997.

[3] T. Sogabe, et al., “Iprovement in properties and air oxidation resistance of carbon materials by boron oxide impregnation”, Carbon Vol. 35, No. 1, pp. 67-72,1997

[4] D. J. Allardice and P.L. Walker Jr. “The effect of substitutional boron on the kinetics of the carbon-oxygen reaction”, Carbon, 1970 Vol. 8, pp 375-385.

[5] J. Kane, et al., “An oxygen transfer model for high purity graphite oxidation”, *Carbon*, 59 (2013) 49-64.

[6] M. El-Genk and Jean-Michel P. Tournier, “Development and validation of a model for the chemical kinetics of graphite oxidation”, Journal of Nuclear Materials 411 (2011) 193–207.

[7] P. Winston and J. Sterbentz, “Oxidation resistant additions in nuclear graphite,” IDR-BA-785.

[8] P. Winston, J. Sterbentz, and W. Windes, “Inhibition of Oxidation in Nuclear Graphite,” SMINS 2013 proceedings, September 2013.

[9] Rebecca E. Smith, *Status of Graphite Oxidation Work*, INL/EXT-10-18880, May 2012.

[10] B. T. Kelly, “Physics of Graphite,” *Applied Science Publishers*, 1981, pp 477.