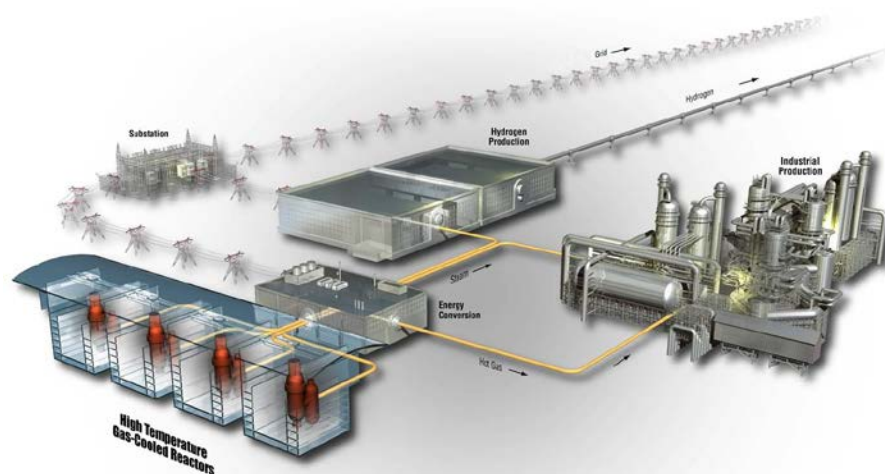# Effects of Oxidation on Oxidation-Resistant Graphite

W. Windes, R. Smith, and M. Carroll

April 2015

Idaho National Laboratory

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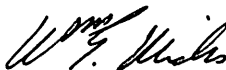
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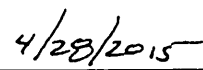
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INL/EXT-15-35050
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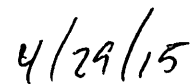
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ABSTRACT

The Advanced Reactor Technology Graphite Research and Development Program is investigating doped nuclear-grade graphite that exhibit oxidation resistance through formation of passive protective oxides on the surface of the graphite material. In the unlikely event of an air-ingress accident, graphite components within the very high-temperature reactor core region are anticipated to oxidize if oxygen enters the hot core region and core temperatures remain above 400°C. For the most serious air-ingress accident, which might persist over several hours or days, continued and progressive 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 ef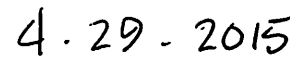fects and keep the core intact. Previous air oxidation testing of nuclear-grade graphite doped with varying levels of boron-carbide (B_4C) at a nominal 739°C was conducted for a limited number of doped specimens and demonstrated a dramatic reduction in oxidation rate compared to similar unboronated-grade graphite. This report summarizes the conclusions from this small scoping study by determining the effects of oxidation on the mechanical strength resulting from oxidation of boronated and unboronated graphite to a 10% mass loss level. While the B_4C additive did reduce mechanical strength loss during oxidation, adding B_4C dopants to a level of 3.6% or more reduced the as-fabricated compressive strength nearly 50%. However, the strength for boronated graphite was reduced only 11% after oxidation while unboronated graphite strength was reduced by over 30%. For future work, this report also discusses infusing different graphite grades with silicon- and boron-doped material as a post-machining conditioning step for nuclear components as a potential solution for these challenges.

CONTENTS

FIGURES

TABLES

ACRONYMS

ART   Advanced Reactor Technology

INL   Idaho National Laboratory

R&D   research and development

RSA   reactive surface area

VHTR   very high-temperature reactor

Effects of Oxidation on Oxidation-Resistant Graphite

1.   BACKGROUND

The Advanced Reactor Technology (ART) Graphite Research and Development (R&D) Program is currently studying nuclear graphite doped with material to promote oxidation resistance when exposed to an oxidizing environment. Graphite reactor 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 that allows significant levels of water or air into the graphite core region results in oxidation of the graphite core components. The associated concern is that continued corrosion of the components resulting from an uninterrupted ingress of oxygen may degrade the structural graphite mechanical strength levels and compromise structural integrity of the graphite core during an extended air-ingress accident. Mitigating oxidation of the graphite core material would minimize the structural effects and keep the core intact during an air-ingress accident.

The National Aeronautics and Space Administration and aerospace industry and most recently Idaho National Laboratory (INL) have conducted graphite oxidation-resistant studies on graphite and carbonaceous materials. These studies demonstrated that some oxygen sensitive (oxide forming) dopants added to the precursor mix of engineered graphite grades can significantly reduce the oxidation rate of graphite components.[1,2,3] The dopant additions to the graphite form protective oxide films that shield the bulk graphite from the available oxygen, resulting in a significant decrease in the overall oxidation rate.[4] 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 to 500°C).[5] 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 added element species for a carbon atom within the graphene plane. These substitutional additives 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 that decreases the rate of graphite oxidation. This decrease in oxidation occurs 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).[6,7,8] The physical coverage of the oxide film depends on the additive impurity level and mixing homogeneity during fabrication. While it is impossible to completely cover all RSA sites to halt oxidation, introduction of these locally adherent oxide films can significantly suppress the overall oxidation of 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 dopants form thermally stable oxide films, ranging from 450°C for boron dopants to as high as 1100°C for silicon dopants. An interesting observation for the lower temperature coatings (such as boron oxide or boro-oxycarbides) 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 that forms within the pores of the graphite. At temperatures > 450°C, the atmosphere above these oxy-carbide filled pores tends 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) 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. The isotope ^{11}B with a significantly lower thermal neutron absorption cross section (^{10}B = 7000Barns, ^{11}B = 0.01Barns) has been proposed for use to avoid invoking a significant neutron penalty instead of boron contaminated with the high absorption cross-section of ^{10}B.

While [11]B would impose a limited neutron penalty for core component applications, it has been shown that addition of boron to a graphitic material increases the irradiation damage potential inside the graphite crystal structure.[9] This is due to the increased internal stresses imposed on the crystal structure during the substitution process where boron atoms are allowed to substitute for carbon atoms within the graphitic crystal structure. During neutron induced ballistic events, this increased internal stress energy is released when the boron atoms are removed from the atomic crystal structure creating more damage defects than would normally be expected from irradiation of a pure carbon atom graphitic crystal structure. The increased damage is limited but measurable. Consequently, irradiation material property changes, specifically irradiation induced dimensional changes, can be accelerated with addition of boron to graphite. This increase in damage effects leads to a reduced useful lifetime for core components receiving medium to high levels of dose.

Accelerating irradiation damage imparted on graphite core components would not be practical for long lived core components. However, these doped graphite grades may be acceptable for short lived core components (e.g., fuel elements and fuel matrix material) or components outside the neutron core (i.e., core support structures). While recent INL studies have demonstrated significant oxidation improvements with a doped graphite grade (B_4C additive to 6% by weight), understanding the effects of oxidation on mechanical strength is needed to ascertain whether these materials are viable for low dose or short lived graphite components.

Core components utilizing oxidation resistant graphite are assumed to retain more mechanical strength than unprotected graphite grades during oxidation conditions due to lower degradation of the structural graphite material. This current study completes the initial assessment of oxidation resistant graphite grades by comparing the mechanical strength of graphite with and without the addition of B_4C that have been oxidized to mass loss levels of 10%. These mechanical compression testing results and future plans to utilize new silicon- and boron-graphite grades are discussed in this report.

2.   OXIDATION TESTING OF BORON-CARBIDE GRAPHITE GRADES

A small scoping study with a limited number of B_4C-doped graphite specimens being evaluated as oxidation resistant graphite was conducted in 2014.[4] Similar to previous very high-temperature reactor (VHTR) studies on nuclear grade graphite, oxidation testing was conducted in a vertical oxidation furnace as detailed in ASTM 7542[10] and the previous VHTR report.[11] Oxidation and mechanical testing results were compared for boronated and unboronated graphite to determine the effect of oxidation on these oxidation resistant graphite types.

2.1   Oxidation Testing Procedure

Specimen size, oxidation temperature, and oxidizing environment were duplicated from previous oxidation studies on unboronated graphite to directly compare the oxidation rate between those results and the oxidation behavior of the new boronated graphite grades. Testing was performed under isothermal oxidation conditions at 739°C in 100% air with a 10 L per minute air flow. Mass loss during oxidation was measured after the isothermal oxidizing environment had been established in the vertical furnace (Figure 1). All unboronated specimens were oxidation tested to 1, 5, and 10% mass loss levels in 100% air. Due to the limited material supply of boronated graphite, all boronated specimens were oxidized to a 10% mass loss level in 100% air to produce the maximum change in mechanical strength after oxidation.
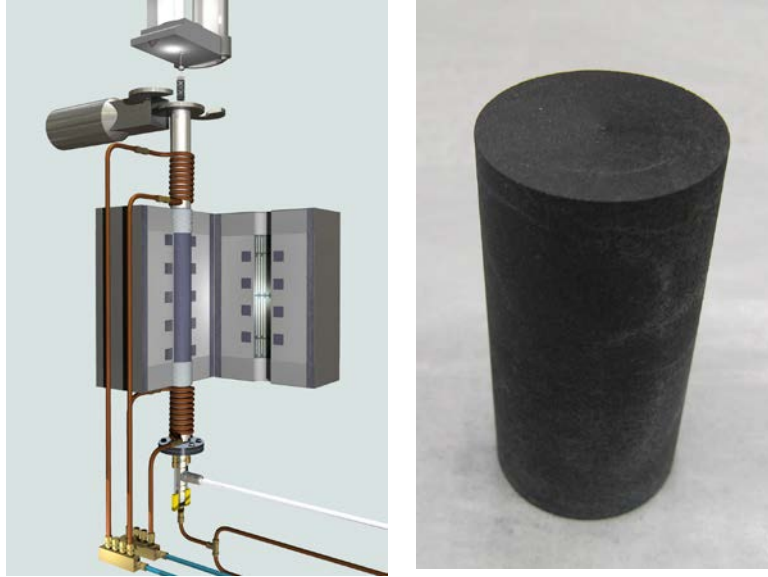
Figure 1. Illustration of vertical oxidation furnace as specified in ASTM 7542 and oxidized boronated specimen.

A limited specimen test matrix was developed for this small study based on available boronated graphite material. Only 16 specimens could be machined from the available material, which was deemed acceptable to determine the basic trend of the protected graphite. The basic specimen test matrix is shown in Table 1.

Table 1. Boronated graphite oxidation specimen test matrix.

Boron Content (%)	Total Specimens	Unoxidized Specimens	Oxidized Specimens
0	16	3	13
3.6	5	2	3
4.9	7	4	3
5.9	4	2	2

While the specimen diameter was kept consistent with suggested values in ASTM 7542, the specimen size was longer than suggested to allow direct compression testing of the specimen after oxidation. Specimen dimensions of 25.4 mm in diameter by 50.8 mm in length (1 in. in diameter by 2 in. in length) were selected to match the aspect ratio designated in ASTM C695.[12] This specimen size was used previously in INL mechanical testing programs and chosen to directly compare the residual mechanical strength after oxidation of boronated and unboronated graphite grades.

2.2   Oxidation Testing Results

In general, all unboronated graphite grades reached a 10% mass loss within 3 hours at 739°C in 100% air as shown in Figure 2. Figure 3 demonstrates that the addition of boron to the graphite matrix resulted in dramatic reductions to the oxidation rate when compared to the unboronated graphite grades. The oxidation rate decreases rapidly as the boron content is increased, with the 5.9% B_4C doped graphite observed to react at onetwentieth the rate of the unboronated graphite grades.
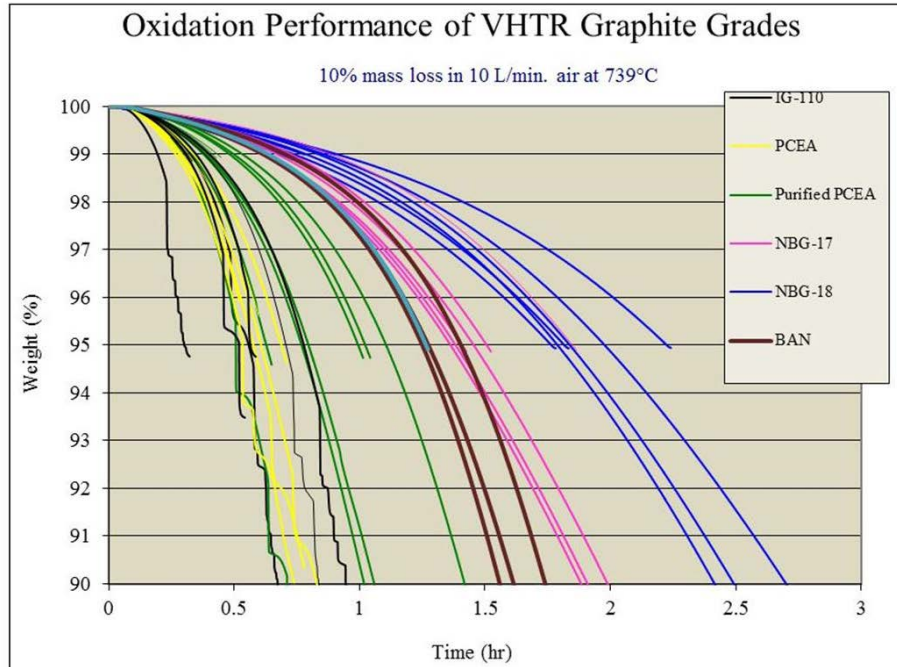
Figure 2. Oxidation performance of Very High-Temperature Reactor graphite grades from previous studies (unboronated).
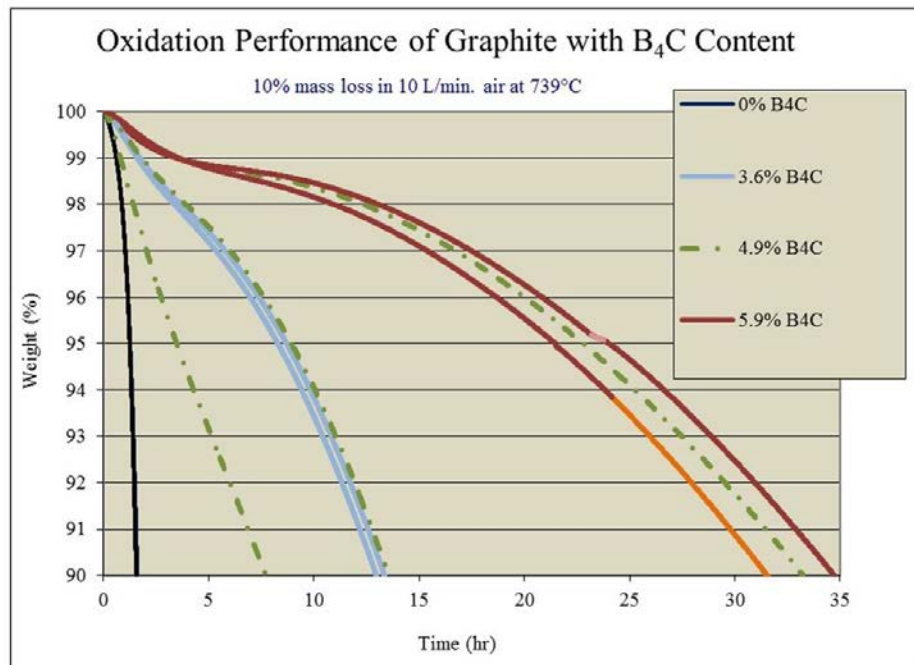
Figure 3. Oxidation performance of boronated graphite.

As discussed in INL/EXT-14-32513, the formed oxide film does not completely halt oxidation of the graphite; the rate is just reduced dramatically. This results from lack of a contiguous film formed for these relatively low boron content graphite grades. In addition, these B_4C-doped graphite specimens exhibited less than consistent oxidation performance or uniform oxide film formation. This inconsistent film formation and oxidation rate is readily demonstrated by the 4.9% B_4C specimens. As shown in Figure 3,

the three 4.9% B_4C specimens exhibited very different oxidation rates for specimens with similar B_4C content but derived from different fabrication batches. During post-oxidation inspection, the visible film at the surface of the specimens differed dramatically between the higher and lower oxidation rate specimens (Figure 4). This was explained by fabrication of the graphite billets within a small, development process line that was used for prototype-grade materials. Perfect uniform mixing and distribution of the additives is difficult to achieve in these small mixing batches proving a challenge to produce consistent material throughout the formed billets. Inconsistency issues were further exacerbated as the 4.9% B_4C specimens were machined from billets fabricated in two separate batches. Different mixing, billet formation, and even graphitization of these billets would tend to magnify varying responses from these small batches of B_4C-doped graphite.

(a)   (b)   (c)
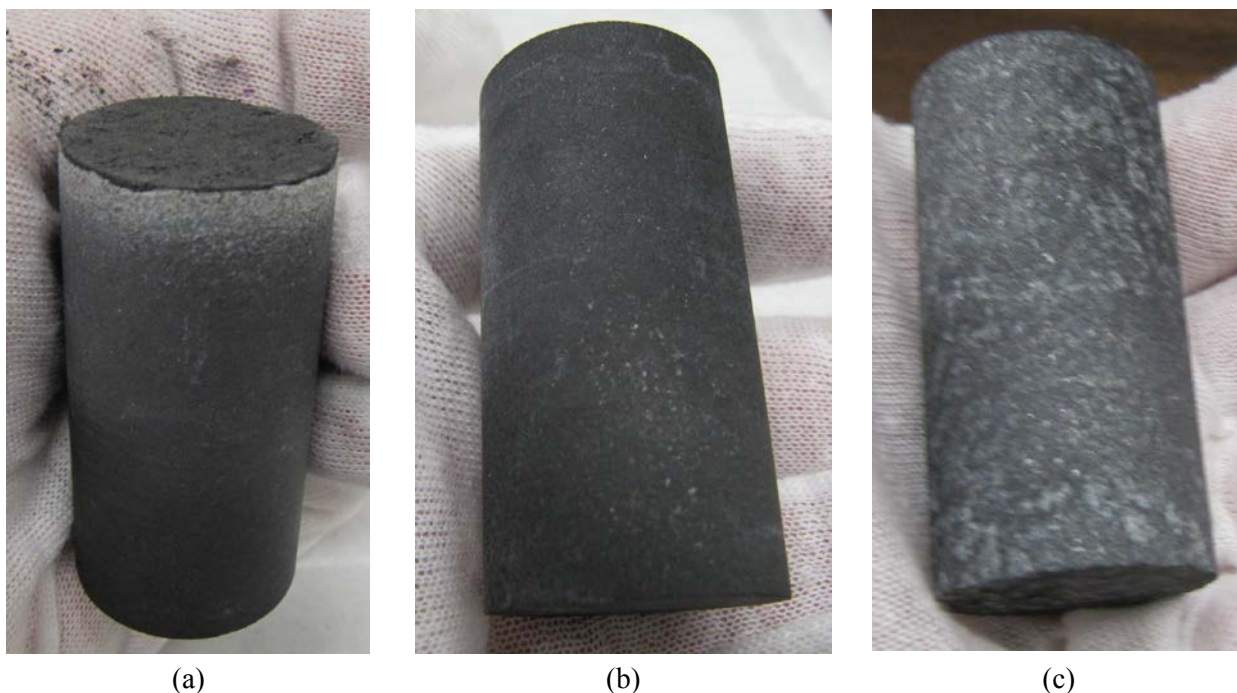
Figure 4. Oxide film formation on 4.9% B_4C additive graphite grades. Oxide films shown in (a) are not apparent except on very bottom edge with a highly oxidized end, (b) some oxide film formation but it is inconsistent and not uniform across surface area, and (c) large adherent oxide film formation for 4.9% B_4C specimen with lowest oxidation rate.

As seen, the formation and behavior of the oxide film on the surface of these resistant graphite grades is difficult to predict. Oxide films formed at high temperatures appear stable and resistant to thermal degradation at least to temperatures of 739°C. However, one of the boronated specimens was initially only oxidized to 5% mass loss to inspect the oxide film formation at lower mass loss levels. After measuring the test specimen dimension, the specimen mass was re-measured and found to have gained 0.06 g from the mass measured directly after oxidation testing. This weight gain is assumed to have occurred from adsorption of oxygen and water from the surrounding atmosphere to the oxide film formed previously on the graphite specimen. This corresponds to a general trend where specimens with higher B_4C loading exhibited higher mass loss after conditioning (i.e., drying) the specimens at 120°C for 3 hours before oxidation testing. Conditioning specimens with larger B_4C levels resulted in a weight loss of 0.007 g, while specimens with the lowest B_4C levels only lost 0.003 g.

The 0.06 gram weight gain observed is likely accentuated oxygen pick-up (either molecular oxygen and/or moisture from surrounding ambient air) accelerated by the previous oxidation testing to 5% mass loss. It is assumed that oxidizing the available carbon atoms both on the specimen surface and along diffusion pathways inside the graphite microstructure exposed higher concentrations of boron. Exposing larger amounts of the substitutional boron allows greater oxidation and/or water adsorption to occur which will mask available RSA sites. The implication from these weight gain observations is that only minimal conditioning may be required to form an oxide layer on these oxygen sensitive additives to the oxidation-resistant graphite grades. Once a boronated graphite component has been machined to tolerance it may be treated in a modest 100 to 120°C dry air atmosphere to initialize the growth of a protective oxide film which could provide immediate protection during an air ingress event. Any oxides formed would need to be thermally stable which may be possible if they were initially formed in a dry air environment and exposed to normal operating conditions of 900-1100°C. The formation, stability, and protection of any oxides formed after such a conditioning step would require further investigations.

Finally, boron is a powerful sintering aid for graphite fabrication. Similar to boron as a micro-hardener in steels, even low levels of boron can significantly change the microstructure of graphite during fabrication. It was observed that addition of B_4C significantly increased the resistance to abrasion and wear during machining. These microstructural changes are expected to result in dramatic changes to the mechanical properties of the formed graphite. Mechanical testing is required to determine the effects of boron addition on the mechanical strength of nuclear-grade graphite before and after oxidation.

3. MECHANICAL STRENGTH TESTING OF BORON-CARBIDE GRAPHITE GRADES

Mechanical testing of the previously oxidized boronated and unboronated graphite was conducted to compare strength changes to the graphite after oxidation. Compression testing of a borated and unboronated graphite grade specimen was conducted similar to previous mechanical testing in the ART Graphite R&D Baseline Program.

3.1   Mechanical Strength Testing Procedure

The ART Graphite R&D Baseline Program establishes the statistical non-irradiated thermo-mechanical and thermo-physical properties of nuclear grade graphite.[13,14] By characterizing lot-to-lot and billet-to-billet material properties of multiple graphite grades, the program assesses the maximum variations in these properties for probabilistic baseline data needs and provides a significant amount of comparative data from which to evaluate other types of graphite mechanical performance. Tensile, compression, and flexural strengths are analyzed using American Society for Testing and Materials International methods identified as standard practices for testing graphite components for use in high-temperature gas-cooled reactors. For assessment of oxidation effects, compression testing utilizing ASTM C695 was used to compare the mechanical property changes for oxidized specimens.

All test specimens were initially machined to dimensions of 25.4 mm in diameter by 50.8 mm in length (1 in. in diameter by 2 in. in length). These dimensions comply with the guidelines set forth in the applicable sections of ASTM C695 and are similar to specimen dimensions in previous INL baseline compression testing.[15] While the specimen diameter was kept consistent with suggested sample sizes prescribed in ASTM 7542, the specimen size was longer than suggested to allow for direct compression testing of the specimen after oxidation.

All specimens were tested with an Instron 5582 electromechanical test frame using Instron's Bluehill™ software suite for test control and raw data generation. Specimens were loaded to failure at 1.00 mm/min, with strain recording via a deflectometer measuring movement of the upper compression platen. The strain measuring system was calibrated to a measuring range that exceeds the largest strains or deflections expected in the test profile being performed. Calibration and use of the strain-measuring devices were documented in applicable sections of PLN-3347[16] or ASTM E83.[17]

3.2   Mechanical Strength Testing Results

As expected, at greater oxidation levels (higher mass loss), the compressive strength of the unboronated nuclear-grade graphite was reduced as shown in Figure 5. The average compressive strength for unoxidized graphite was comparable to other nuclear-grade graphite tested within the ART Graphite R&D Baseline Program,[15] but strength was reduced (11 to 32% for high-temperature oxidation and 53% for lower-temperature oxidation) as the graphite was subjected to higher mass loss levels (Table 2).
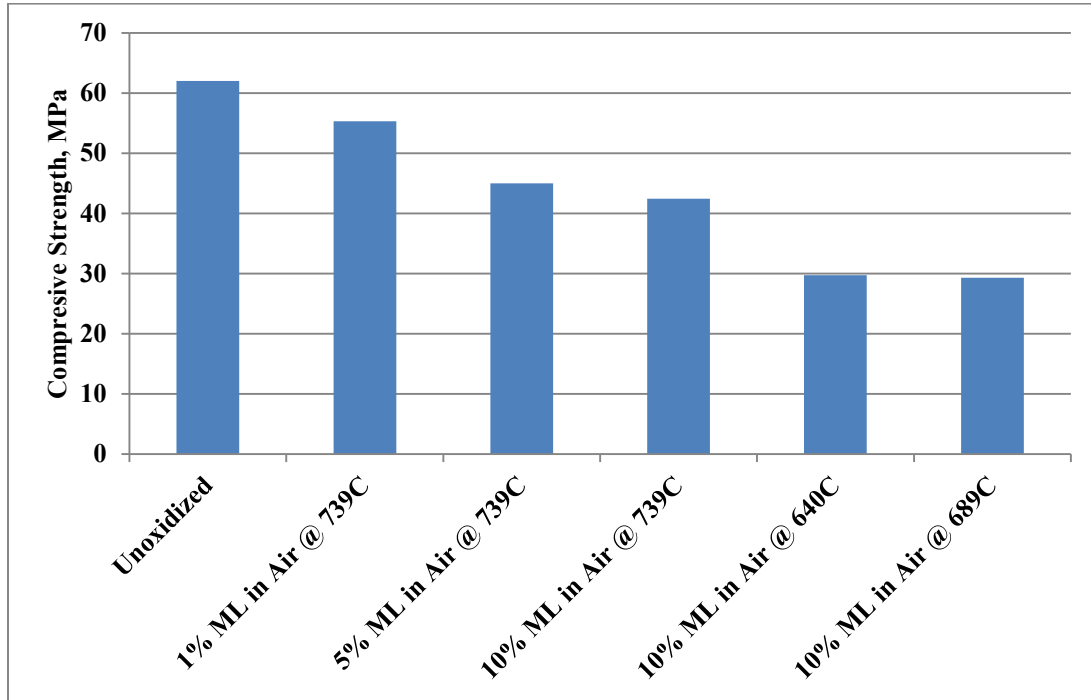
Figure 5. Compressive strength changes for graphite oxidized to 0, 1, 5, and 10% mass loss levels. Note that specimens oxidized at lower temperatures to 10% mass loss demonstrate lower strength.

Table 2. Oxidation response of unboronated nuclear-grade graphite.

Strength Changes Oxidized at	0% ML	1% ML	5% ML	10% ML (739°C)	10% ML (<739°C)
739°C	—	11%	27%	32%	53%
689°C	—	—	—	53%	—
640°C	—	—	—	52%	—

Of note, unboronated specimens oxidized at lower temperature have a lower mechanical strength than comparable mass loss specimens oxidized at higher temperatures. This illustrates the differences in oxidation behavior between the kinetically-controlled oxidation regime (lower temperature regime) and diffusion controlled regime (higher temperature regime). Exposure at the relatively low temperature limits the oxidation rate for the graphite-oxygen reaction thus allowing the oxygen to diffuse into the interior of the graphite through the open pore structure inherent to nuclear grade graphite. Oxygen diffusion into the internal microstructure causes internal oxidation and reduces more of the effective load bearing volume of the graphite than if the graphite had been oxidized off the surface of the specimens.

For higher temperature oxidation (diffusion controlled regime), the oxidation rate is fast enough that the majority of the oxygen is reacted at or near the surface leaving the interior microstructure intact. Only a relatively thin skin of material was oxidized from these higher temperature specimens leaving a larger effective load bearing volume for specimens that have been corroded to similar mass loss levels. Since a larger effective load bearing volume is present, the specimens oxidized at a higher temperature demonstrated more strength than those specimens oxidized at lower temperatures with corroded interior microstructure.

As shown in Figure 6, the addition of B_4C additives significantly altered the mechanical strength of the graphite both before and after oxidation. The addition of B_4C to the nuclear-grade graphite resulted in approximately a 50% reduction in strength to the nuclear grade graphite with higher levels of B_4C yielding lower overall mechanical strength (Table 3). This is a significant reduction in the unoxidized compressive strength of the graphite and would impact any structural component made from this grade.
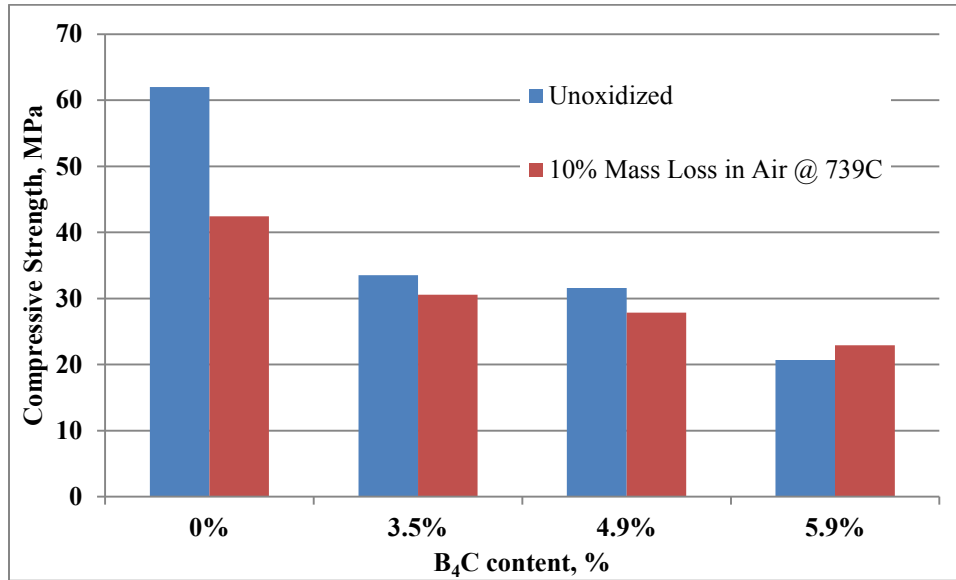
Figure 6. Compressive strength values for unoxidized and oxidized (10% mass loss) specimens.

Table 3. Compressive strength changes for boronated and unboronated graphite.

	B_4C Content			
	0%	**3.6%**	**4.9%**	**5.9%**
Strength changes from B_4C addition	—	−45.9%	−49.1%	−66.6%
Strength changes resulting from oxidation	−31.5%	−8.8%	−11.8%	+10.6%
Oxidized strength differences from 0% B_4C addition	—	28%	34%	30.7%

However, as predicted, the protected graphite grades demonstrated less strength loss due to oxidation than the unprotected graphite. The 3.6 and 4.9% B_4C grades were reduced only approximately 10% versus a strength reduction of approximately 31% for the unprotected graphite. The 10.6% strength increase for the oxidized 5.9% B_4C grade is most likely due to inconsistencies in fabrication noted previously without the ability for an outlier correction owing to the extremely low number of test specimens for this limited scoping study. However, the trend of higher post oxidation strength is preserved illustrating that greater levels of protective additives will provide more oxidation protection.

Unfortunately, even the relatively modest levels of boron additive (3.6 to 5.9% B_4C) result in such a large reduction in mechanical strength that any protection provided by the additive is minimized. All boronated grades demonstrated less unoxidized strength than the oxidized unboronated grades. Since the compressive strength of the unboronated grade was nearly a factor of 3 larger than the boronated grades, even the reduced oxidized strength of the unboronated graphite was higher than any of the unoxidized B_4C-doped grades. Clearly, these levels of B_4C additives provide excellent oxidation protection and strength retention but the loss in overall unoxidized strength resulting from the additives may be prohibitive for structural components in nuclear applications.

Despite this concern with the lower initial strength, it should be noted that the demonstrated higher strength retention of oxidized boronated graphite increases the structural performance predictability of nuclear components made from this grade. Strength changes are much larger for oxidized unboronated graphite, which imposes a larger range of retained strength in nuclear components. This reduces the ability of component designers to predict the structural stability of unboronated graphite after oxidation has occurred. While the initial strength of the boronated material is smaller than normal nuclear graphite grades, this issue can be resolved through design changes (e.g., larger core support columns) to take advantage of the increased strength predictability. If the boronated graphite strength is determined to be sufficient to meet the structural requirements, with modest design changes, the increased predictability and performance of these components during an oxidation event may make this material desirable for future high-temperature reactor applications.

Compression strength results for all specimens tested in this scoping study are provided in Appendix A and Appendix B.

4. CONCLUSIONS OF B_4C-DOPED OXIDATION—RESISTANT GRAPHITE

As demonstrated previously in oxidation report INL/EXT-14-32513,[4] doping nuclear-grade graphite with B_4C significantly reduces oxidation rates for graphite at relatively high temperatures and high oxygen levels. Boronated graphite with nearly 6% by weight B_4C was observed to react at one-twentieth the rate of the unboronated graphite for the first 10% loss of mass.

Observations during machining of these boron additive grades showed that while the overall hardness of the graphite was increased with increasing levels of B_4C, mechanical testing demonstrated that the addition of B_4C results in a significant overall reduction in strength to the nuclear grade graphite. This may be attributed to a number of factors including loss of adherence between graphite crystallites due to boron substitution to the graphitic crystal structure, physical stress (and strain) on the microstructure due to the addition of boron, or less crack deflection and/or lower crack formation energy required to propagate through the much harder (brittle) microstructure. The reduction in strength may be mitigated by lowering the levels of B_4C addition but less protection is anticipated as a consequence.

While strength reduction is problematic, oxidation protection is also significant for these boronated grades. A twentyfold decrease in oxidation rate plus a threefold increase in strength retention after oxidation when compared to the unboronated grade would greatly increase the structural safety margin of nuclear grade graphite components. If strength reduction can be minimized while still maintaining oxidation protection, this oxide forming additive could be an important consideration for future graphite fabrication processes in nuclear component designs.

Finally, while B_4C provides excellent oxidation protection for graphite, the protective oxide will eventually start to degrade when temperatures approaching 1000 to 1100°C, depending on the pore structure on the graphite surface. If the anticipated temperature is much higher, using silicon carbide 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). Similar challenges to machining (hardness increase), strength reduction, and fabrication consistency issues are anticipated for silicon-carbide-doped graphite as well. As a result, a methodology for providing a protective layer after machining that minimizes the strength changes is required before any immediate changes to nuclear grade graphite can be suggested.

5. FUTURE ACTIVITIES IN OXIDATION-RESISTANT GRAPHITE GRADES

Issues with fabrication, additive consistency, machining, and strength reduction are major considerations for viability of oxidation resistant graphite grades. As discussed here and in INL/EXT-14-32513, commercial fabrication of doped graphite is difficult as 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. Contamination problems can be resolved through a separate fabrication line, thus eliminating the spread of contamination to other graphite grades and resolve additive distribution and consistency issues in billet fabrication. However, this is an expensive and time-consuming solution and will only occur if there is a major market for such a product.

Unfortunately, machining and strength reduction issues for doped material are pervasive to the fabrication process itself. As discussed, significant oxidation protection only occurs when the additive dopant (boron, silicon, phosphorus, etc.) substitutes itself into the graphene plane structure providing maximum thermal stability. The substitution process creates significant internal stresses within the crystal structure and, in the case of boron, lead to large increases in the hardness of the material. This decreases the machinability and mechanical strength of the graphite considerably reducing the attractiveness of the oxidation protection.

Taking all issues into consideration, a treatment process *after* final component machining that is relatively cheap, is simple to perform, and maximizes the oxidation protection of graphite while having a minimum effect on component strength, must be considered. These issues have prompted development in oxidation resistant coatings on graphite components. While this is one method for achieving oxidation protection, there are numerous difficulties associated with developing an adherent robust coating that can survive the entire life-time of a nuclear component. A simpler process may be to treat the outside surface of the finished component diffusing a dopant material onto the surface and into the pore structure of the graphite.

A surface infiltration process has the advantage that it can be applied to the final machined component precluding the difficulties in machining a hardened material. Consistency in billet fabrication is increased since there are no additives to change the powder rheology or thermal processes. Finally, by infiltrating and treating a thin outer shell of graphite with oxide forming additives, a protective oxide can potentially form on the outer component surface while the majority of the load bearing volume retains the original structural strength of the graphite grade, uncompromised by the substitution of the protective additive elements.

This surface infiltration methodology appears to be a good compromise in mitigating the strength and machinability issues for additives to the entire batch process and providing oxidation protection on the exterior of nuclear components. INL will conduct a series of small scoping studies to explore the viability of this infiltration methodology and ascertain possible surface treatments that can diffuse additive materials into the graphite structure. Liquid and gas infiltration methods will be employed to infiltrate the

two most favorable dopants into graphite specimens: boron and silicon. While other dopants such as phosphorous, germanium, and aluminum can also provide oxidation resistance to graphite, the stability of the oxides under irradiation and temperature have been shown to be lower than silicon and boron oxides.

Following successful infiltration of a doped material, the oxidation resistance and mechanical properties of these new graphite grades will be compared to the results found for the B_4C-additive graphite grades reported here. If successful, it is anticipated that silicon- or boron-doped graphite can provide significant oxidation resistance on the outer surface of the component while minimizing issues surrounding machinability, strength reduction, and enhanced irradiation damage.

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7.   APPENDIXES

Appendix A, Compression Test Results for Unboronated Graphite

Appendix B, Compression Test Results for Boronated Graphite

Appendix A

Compression Test Results for Unboronated Graphite

Specimen Label	Diameter (mm)	Anvil Height (mm)	Compressive Stress at Maximum Load (MPa)	Compressive Load at Maximum Load (N)	Displacement (Strain 1) at Maximum Load (mm)	Temperature (°C)	Humidity (%)	Comments
BAN#1	25.4	50.8	43.371	21980	-2.277	22	19	10% ML in air at 739°C
BAN#2	25.4	50.8	47.931	24290	-2.423	22	19	10% ML in air at 739°C
BAN#3	25.4	50.8	36.059	18270	-2.11	22	19	10% ML in air at 739°C
BAN#4	25.4	50.8	45.864	23240	-1.668	22	19	5% ML in air at 739°C
BAN#7	25.4	50.8	37.997	19250	-1.681	22	19	5% ML in air at 739°C
BAN#8	25.4	50.8	51.152	25920	-2.302	22	19	5% ML in air at 739°C
BAN#5	25.4	50.8	45.78	23200	-1.32	22	19	1% ML in air at 739°C
BAN#6	25.4	50.8	64.332	32600	-2.173	22	19	1% ML in air at 739°C
BAN#9	25.4	50.8	55.779	28260	-1.583	22	19	1% ML in air at 739°C
BAN#11	25.4	50.8	28.234	14310	-1.854	22	19	10% ML in air at 689°C
BAN#15	25.4	50.8	30.367	15390	-1.848	22	19	10% ML in air at 689°C
BAN#13	25.4	50.8	30.08	15240	-1.317	22	19	10% ML in air at 640°C
BAN#18	25.4	50.8	29.425	14910	-1.326	22	19	10% ML in air at 640°C
BAN#30	25.4	50.8	49.201	24930	-1.557	22	19	Unoxidized
BAN#31	25.4	50.8	69.241	35080	-2.026	22	19	Unoxidized
BAN#32	25.4	50.8	67.542	34220	-2.051	22	19	Unoxidized

Appendix B

Compression Test Results for Boronated Graphite

Specimen Label	Diameter (mm)	Anvil Height (mm)	Compressive Stress at Maximum Load (MPa)	Compressive Load at Maximum Load (N)	Displacement (Strain 1) at Maximum Load (mm)	Temperature (°C)	Humidity (%)	Comments
BA4B4C#1	25.4	50.8	30.822	15620	-1.768	22	19	10% ML in air at 739°C
BA4B4C#2	25.4	50.8	28.988	14690	-1.119	22	19	10% ML in air at 739°C
BA4B4C#3	25.4	50.8	38.562	19540	-2.045	22	19	Unoxidized
BA4B4C#4	25.4	50.8	38.812	19670	-2.122	22	19	Unoxidized
BA4B4C#5	25.4	50.8	31.918	16170	-1.295	22	19	10% ML in air at 739°C
BA5B4C#1	25.4	50.8	29.564	14980	-2.505	22	19	10% ML in air at 739°C
BA5B4C#2	25.4	50.8	28.733	14560	-1.219	22	19	10% ML in air at 739°C
BA5B4C#3	25.4	50.8	35.523	18000	-1.721	22	19	Unoxidized
BA5B4C#4	25.4	50.8	39.574	20050	-1.482	22	19	Unoxidized
BA5B4C#5	25.4	50.8	29.868	15130	-1.372	22	19	10% ML in air at 739°C
BA5B4C#6	25.4	50.8	23.252	11780	-1.257	22	19	10% ML in air at 739°C
BA5B4C#7	25.4	50.8	19.624	9943	-1.499	22	19	Unoxidized
BA6B4C#1	25.4	50.8	29.409	14900	-1.429	22	19	5 + 10% ML in air at 739°C
BA6B4C#2	25.4	50.8	22.898	11600	-1.322	22	19	10% ML in air at 739°C
BA6B4C#3	25.4	50.8	20.477	10380	-1.849	22	18	Unoxidized
BA6B4C#4	25.4	50.8	20.916	10600	-1.712	22	18	Unoxidized