

THE CHARACTERIZATION OF HIGHLY CRYSTALLINE, ISOTROPIC GRAPHITE

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Abstract

A novel, low CTE, highly isotropic isostatically molded grade of graphite has been produced and characterized. This graphite has been manufactured using a raw needle coke and utilizes boron as a graphitization catalyst. Physical and chemical property data as well as microscopic structural characterization will also be presented.

Introduction

Elemental doping of carbon and graphite materials has been a topic of research and development interest for many years. Doping with both metal and non-metal impurities has been shown to have a drastic effect on the electronic, thermal and physical characteristics of the resulting material. Specifically, the use of boron as a dopant has been investigated to alter the electronic band structure and thermal conductivity of carbon-based materials ranging from fullerenes and single and multiwalled nanotubes to pyrolytic graphite. Boron is also a well-known graphitization catalyst, lowering the threshold temperature for conversion from 2-D carbon to 3-D graphite. While there is a significant amount of data published on the doping of carbon-based materials, there is little information published where boron is introduced into bulk monolithic graphite produced in relatively large quantities.

The objective of this study is to utilize the catalytic effect of boron in graphite to increase crystallinity, isotropy and resistance to oxidation, and to decrease the coefficient of thermal expansion. The combination of these properties may be ideal for a number of applications, including potential use for high temperature nuclear reactor designs where a high degree of isotropy is desirable.

The work presented here utilizing a combination of raw material selection, forming method, and catalyst additive is the first known published work of this nature.

Experimental

Graphite Manufacture

The graphite produced for this study was manufactured using a milled (<44 μm), raw needle coke as a filler material. The filler coke was mixed with varying concentrations of boron carbide, and then combined with a coal tar binder pitch. The resulting material is formed via isostatic molding, then carbonized. A densification step was done prior to final heat treatment.

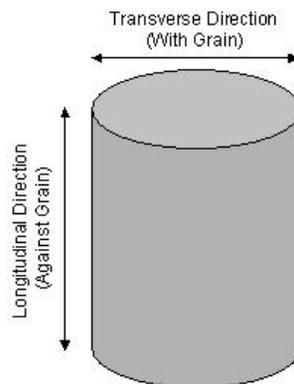


Figure 1. Relationship of forming axes and grain direction for typical isomolded graphite.

Isostatic molding generally leads to a product with particles aligned transverse to the mold filling direction. This leads the preferred orientation of the crystalline “a” axis to be in the transverse direction. Figure 1 illustrates conventional terminology where the “transverse” direction is also the “with grain” direction. In this study, the

catalytic effect of boron had a stronger influence on preferred orientation than any identified processing variables. The relationship between the “with” and “against” grain directions and the orientation of test specimens can be reversed from conventionally manufactured graphite. To be consistent, test sample orientation will only be discussed in terms of the longitudinal and transverse directions.

Results and Discussion

Physical Properties

Table 1 shows a comparison of the physical properties of un-doped and boron-doped graphite. The boronated graphite was manufactured with 3 varying dopant concentrations ranging from 4 wt.% to 5.5 wt.%. Boron is accommodated into the graphite lattice in substitutional sites with a maximum solubility of approximately 2.35 at %. Excess boron is believed to be present in the form of boron carbide.

Table 1. Physical Properties Characteristics of Un-doped and Boron-doped Graphites

| | | 0% Boron | | 4.0 % Boron | | 5% Boron | | 5.5% Boron | |
|-----------------------------|--------------------------------------|------------|--------------|-------------|--------------|------------|--------------|------------|--------------|
| | | transverse | longitudinal | transverse | longitudinal | transverse | longitudinal | transverse | longitudinal |
| Density | g/cc | 1.72 | | 1.7 | | 1.65 | | 1.71 | |
| Flexural Strength | MPa | 28 | | 30 | 34 | 21 | 20 | 15 | 15 |
| Young's Modulus | GPa | 7.9 | | 16 | | 15 | | 18 | |
| Specific Resistance | $\mu\Omega m$ | 7.3 | | 8 | | 9 | | 9.7 | |
| CTE (30-100 °C) | $\times 10^{-6}/C$ | 3.8 | 5.1 | 1.22 | 2.01 | 0.90 | 1.41 | 0.55 | 0.54 |
| CTE Isotropy Ratio | | 1.34 | | 1.64 | | 1.55 | | 0.98 | |
| Thermal Conductivity | W/mK | 130 | | 82 | 72 | 68 | 66 | 66 | 65 |

The measured decrease in the CTE of catalyzed graphite is well documented by a number of authors. However, the drastic decrease by nearly an order of magnitude in the measured CTE reported here is novel. In addition, the high degree of isotropy measured has not been previously reported. Table 2 compares the CTE and CTE isotropy ratios for anisotropic and isotropic nuclear graphite with electrode grades. The boron-doped catalytic graphite (the subject of this work) is added to the table for comparison. The isotropy ratio of the catalytic graphite is closest to isotropic nuclear graphite, but has the advantage of a significantly lower CTE.

Table 2. Comparison of the CTE and CTE Ratio of Nuclear Graphite, Electrode Graphite and Catalytic Graphite.

| Graphite Grade | CTE (wg) | CTE Ratio ag/wg |
|---------------------------------------|-----------------|------------------------|
| Anisotropic Nuclear Graphite | 2.2 | 1.73 |
| Isotropic Nuclear Graphite | 5.3 | 1 |
| Electrode Graphite | 0.6 | 2.33 |
| Electrode Graphite Connecting Pins | 0.3 | 7.33 |
| Catalytic Graphite (this work) | 0.55 | 0.98 |

A significant decrease in flexural strength is measured with increasing boron concentration and is correlated with the increase in crystallinity.

The Young's modulus of the boronated graphite is significantly higher than that measured for the undoped graphite. We postulate that the Young's modulus for the graphite artifact increases with increasing dopant concentration due to the relatively high modulus inherent to the boron dopant. The published value for the Young's modulus of B₄C ranges from 450 – 470 GPa, significantly higher than the Young's modulus for the undoped graphite.

The electrical characteristics of boron-doped graphite have been extensively studied by Mele and Ritsko and more recently by Endo et al. It is well understood that boron acts as an electron acceptor, thus producing vacancies near the top of the valence band. The result is a lowering of the Fermi level, and a measured decrease in the electrical conductivity.

Thermal and Oxidative Characteristics of Boron-Doped Graphite

The room temperature thermal conductivity for each of the doped graphite materials was compared to the control graphite. A significant decrease in the measured thermal conductivity is observed with increasing dopant concentration. This effect is attributed to the structural modifications that occur when impurity atoms are bound within the substrate lattice. Significant disruption of conduction pathways occurs with the relatively large dopant concentration used for this work.

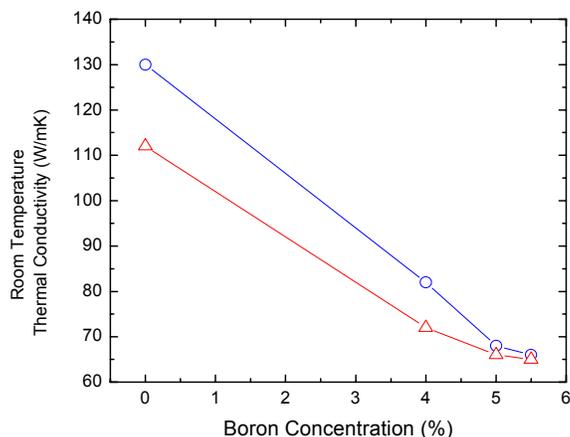


Figure 2. Thermal conductivity of graphite product as a function of boron concentration.

The oxidation behavior of the graphite studied in this work is profound. Figure 3 depicts a comparison of the oxidation behavior for undoped and doped (2 concentrations) and compares it with a typical isomolded graphite product. The boron-doped graphite shows an order of magnitude improvement in the resistance to oxidative attack. Three mechanisms exist to explain the reactivity of boronated materials in an oxidative environment. The first mechanism involves the effect of substitutional boron as an electron acceptor in the graphite matrix. The presence of the boron atom decreases the free electron concentration, thus weakening the bond strength between exposed carbon atoms and adsorbed oxygen. The result is a decrease in the oxidative capacity of the carbon atom. The second mechanism deals with the ‘poisoning’ of active oxidation sites with boron oxide. Due to the large concentration of boron used in this work, we postulate that both mechanisms may apply. The third mechanism explains that due to the improved crystallinity, fewer defective sites that are susceptible to oxidation exist.

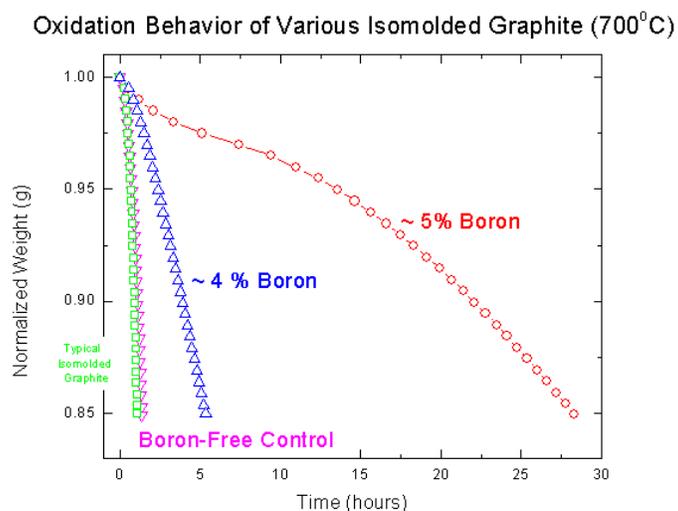


Figure 3. Comparison of the behavior of various doped and un-doped graphites in an oxidizing atmosphere (air, 9L/min.) at elevated temperature (700 °C). Both boron-doped materials show significant resistance to oxidation.

Structural Characterization

Figure 4 shows a comparison of the doped and undoped graphite. The effect of the catalyst on the graphite structure is rather pronounced, revealing an increase in the size of the optical domains and degree of order. The particles seen in Figure 4a are completely replaced by catalytic graphite in Figure 4b.

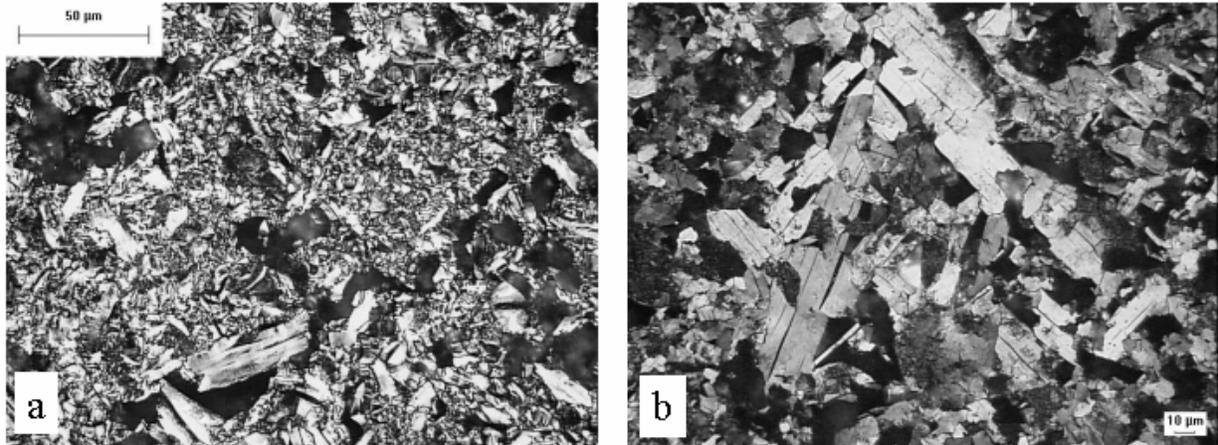


Figure 4. Comparison of a) un-doped graphite (500x, polarized light) with b) ~ 4.0% boron-doped graphite (400x, polarized light).

Further Processing Studies

Two samples of the boron-doped graphite were heat treated for 2 additional cycles ($> 2500\text{ }^{\circ}\text{C}$) in order to investigate the degree to which the coefficient of thermal expansion could be lowered and the extended catalytic effect on the crystal structure and grain size of the graphite. Table 3 shows the effect of the dopant concentration on the lattice parameters measured by x-Ray diffraction. The interlayer spacing, represented by d_{002} , is significantly lower than reported for typical graphite. This is a well-known effect of catalytic graphitization and has been reported for highly oriented pyrolytic graphite substrates doped with boron. The CTE of both samples (4 % boron and 5% boron) decreased significantly with each successive heat treatment step. After the 3rd heat treatment step, the CTE measured was $0.12 \times 10^{-6} / ^{\circ}\text{C}$ (30 – 100 $^{\circ}\text{C}$) for the longitudinal direction for the sample with 5% boron. Figure 6 clearly depicts the large optical domains associated with both concentrations of doped graphite after successive heat treatment cycles. When compared to the undoped material, the optical domain size of the doped and heat treated samples have increased on average by an order of magnitude.

Table 3. X-ray Diffraction analysis of the 4% boron-doped and 5% boron-doped graphite after thermal cycling.

| | D-Spacing 002 Peak (\AA) | Crystallite Size 002 Peak (L_c), (\AA) | Crystallite Size 110 Peak (L_a), (\AA) |
|----------|--|---|--|
| 4% Boron | 3.348 | 1506 | 637 |
| 5% Boron | 3.348 | >2000 | 528 |

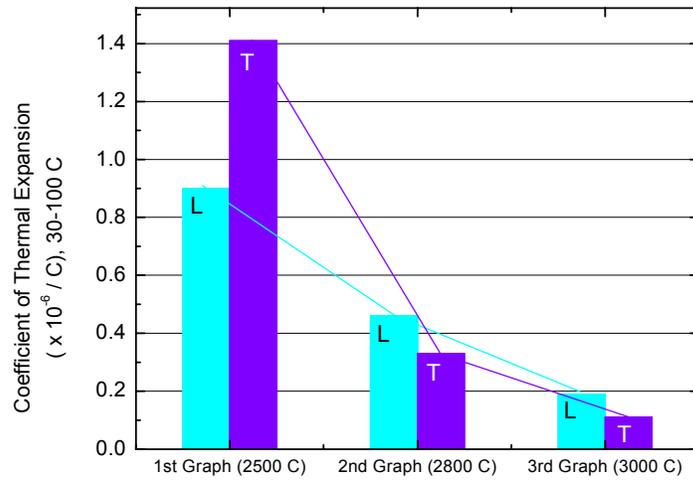


Figure 5. Measured decrease in the coefficient of thermal expansion with additional heat treatment in excess of 2500 °C (4 hour hold at target temperature). This graphite has a nominal boron concentration of ~ 5%. ‘L’ represents the longitudinal direction and ‘T’ represents the transverse direction.

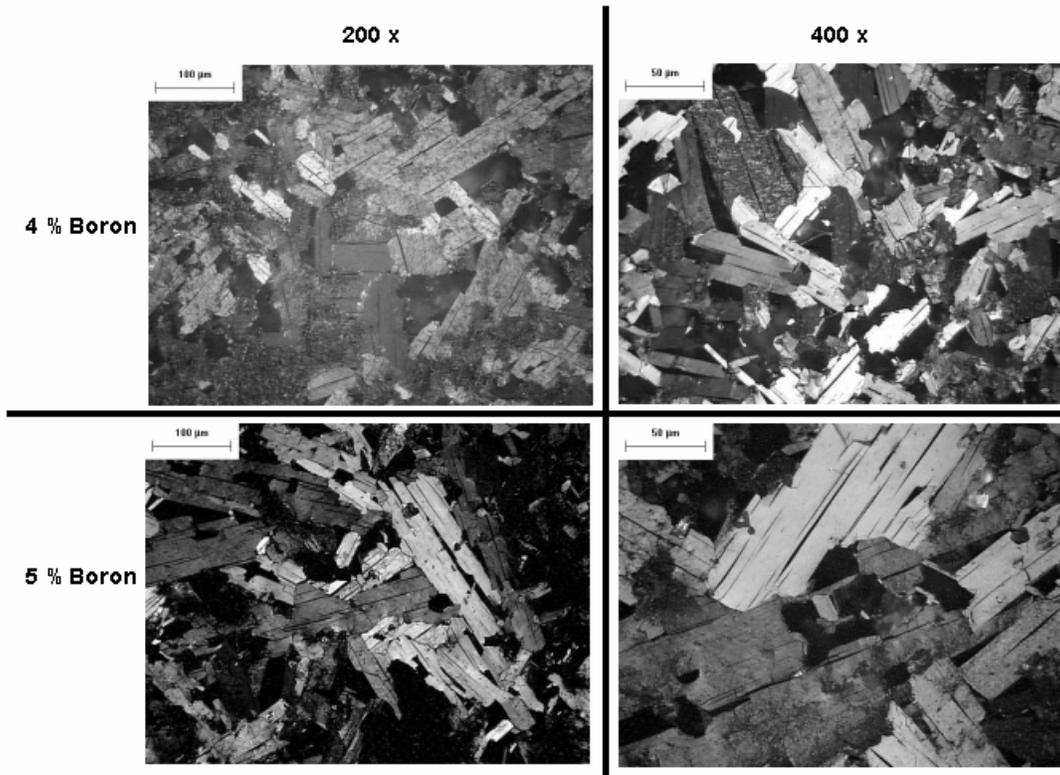


Figure 6. Optical microscopy photographs of specimens from 2 billets that have been heat-treated for three cycles in excess of 2500 °C. The top two images are for specimens with a 4 % dopant concentration. The lower 2 images are for specimens with a slightly higher 5 % dopant concentration.

Summary and Conclusions

A large quantity of highly crystalline, catalytic graphite was manufactured to study structural and property variations with dopant concentration. The resulting product exhibits a high degree of structural order with a very low CTE. This graphite was measured to be resistive to oxidation at 700 °C, prolonging the high temperature lifetime of the material in an oxidative atmosphere. Repeated heat treatment steps reduces the CTE of the material to less than $0.2 \times 10^{-6} / ^\circ\text{C}$ in both orientations and increases the optical domain size within the bulk of the material.

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