OXIDATION INHIBITED BC_X: CHEMISTRY AND STRUCTURE

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INTRODUCTION

Carbon-carbon (C-C) composites are of great importance to the aerospace industry as a thermostructural material [1]. The driving force behind studying structural carbon composites, is the need for materials which have higher specific strengths than conventional aluminum, titanium and nickel based alloys, and can withstand higher use temperatures [2]. Although C-C composites fulfill this need, they oxidize at temperatures in excess of 400°C. One possible solution to this problem is the use of BC_X as an oxidation resistant alternative to carbon-carbon structural materials. The oxidation rates of BC_X coated carbon fibers are less than as - received carbon fibers [3,4].

BC_X is a material with a graphite-like structure containing up to 17% boron in the lattice. This novel compound was first produced in the mid 1980's [5]. The reaction of interest for the synthesis of BC_X is the vapor deposition reaction at 700°C to 1000°C between BCl_3 and benzene to produce a solid boron-carbon film. Benzene rings are linked by boron atoms depositing a hexagonal BC_X structure. The focus of the present work is to model the influence of boron on the BC_X structure.

In previous studies BC_X was modeled as a periodic lattice of stoichiometric composition BC_3 [6,7]. In both studies the structure and electronic structure of BC_3 was investigated. The calculated B-C bond length was found to be ~0.155 nm and the C-C bond length ~0.142 nm. When BC_3 is modeled as a single layer it is calculated to behave as an indirect band gap semi - conductor. However, when BC_3 was modeled as a multi-layered structure it was predicted to behave like a metal which is supported by its metallic appearance [6,5].

COMPUTATIONAL METHOD

All calculations were carried out using the IBM SP2 Supercomputer located at the Cornell Theory Center (Cornell University, Ithaca, New York). The program Mopac 7 was used for all calculations.

Mopac 7 is a semi - empirical molecular orbital package. The Semi - empirical Hamiltonian AM1 (Austin Model 1) is used in the electronic part of the calculation to obtain molecular orbitals, heat of formation, and its derivative with respect to molecular geometry. Molecular orbital parameters for AM1 are optimized so as to reproduce the experimental heat of formation to form a mole of compound at 25°C from its elements in their standard state [8]. The formalism used in AM1 is essentially the same as in MNDO (Modified Neglect of Diatomic Overlap) with the exception of the CRF (Core Repulsion Function) [9].

It is well established that graphite consists of layers of closely bound carbon atoms, while the layers themselves are relatively isolated from one another [10]. BC_X has been shown experimentally to have a layered structure similar to that of graphite [4,5]. The structure being modeled in the present study is of a single BC_X layer. This layer is modeled as a finite cluster with hydrogen at the edges. Three different host lattices were studied: Benzene (C_6H_6), Coronene ($C_{24}H_{12}$), and Circumcoronene ($C_{54}H_{18}$). In each case the host lattice (or molecule) was modeled and used as a "baseline" structure. Then the influence of substituting boron for carbon on selected sites within the host molecule (or cluster) was determined. Finally, evidence of convergence for the model was summarized.

RESULTS AND DISCUSSION

Figure 1 is a computer generated image of a) a benzene host molecule (C_6H_6) and b) a benzene host molecule with boron substituted into the structure at two carbon sites ($B_2C_4H_6$). In comparing the geometry of the two structures it is apparent that the presence of substitutional boron results in distortion of the original host structure. Similar results can be seen in larger molecules as a result of similar substitutional orientations. The distortion of a molecules structure as a result of boron substitution can most easily be observed by overlapping the lattice of the host $C_{24}H_{12}$ molecule with that of a molecule that contains 2 borons substitutionally, as can be seen in Figure 2. It can be clearly seen that the presence of boron in the host molecule results in distortion of that molecule.

In order to validate the current approach for modeling the structure of BC_X, evidence of convergence in the proposed model was sought. It was determined that as the molecule size is increased the percent change in heat of formation from the host molecule to the boron substituted molecule decreased. Such a decrease is evidence of convergence. Secondly, the total energies of the host molecules were compared to the total energies of the boron substituted molecules. In this case the percent change in total energy decreased as the cluster (molecule) size was increased. This is further evidence of convergence in the proposed model. Finally, the electric charge on the substituted boron was studied as a function of molecular size. The electric charge on the substituted boron is plotted as a function of molecular size in Figure 3. It can be seen that the three points can be fit with a logarithmic function

indicating that the charge on boron is converging as cluster size is increased.

CONCLUSIONS

The cluster size convergence with respect to boron substitution heats of formation, total energies, and charges is satisfactory. There are marked differences in the boron - boron interaction for different defect orientations.

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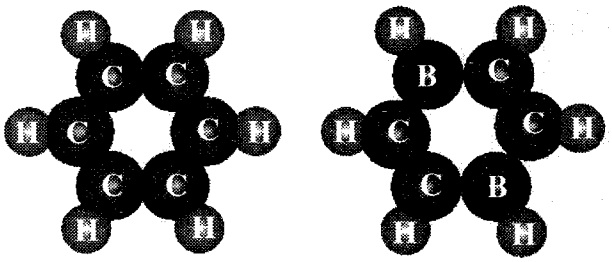

Figure 1 - Computer generated structure of a) Benzene host molecule, b) Benzene host molecule with two borons substituted onto carbon sites.

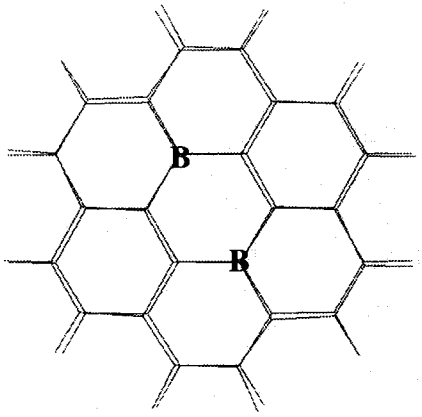

Figure 2 - Computer generated lattice of a $C_{24}H_{12}$ molecule overlapped with the lattice of $B_2C_{22}H_{12}$.

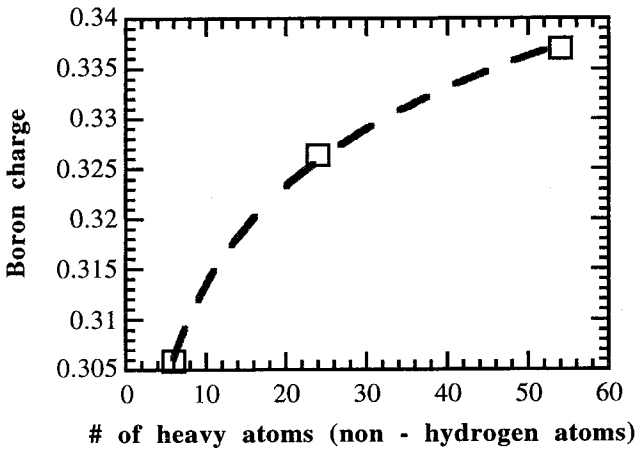

Figure 3 - Charge on boron atoms as a function of the number of heavy atoms (non - hydrogen atoms) in a particular molecule.