The Structure and Oxidation Behavior of the Novel Compound, BCx
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A compound containing boron and carbon was produced via a standard CVD process. BCl3 and C6H6 gasses were reacted at temperatures between 700 and 900 °C to produce films 0.5 to 1.0 microns thick on SiO2 slides and T-300 carbon fibers. It is proposed that this material has a hexagonal, graphite-like structure. XRD has shown the interlayer spacing of this novel compound to be similar to that of graphite (d002 = 0.335 nm). Electron diffraction supports a hexagonal structure as well. Raman spectroscopy indicates a shift in the graphite 1575 cm⁻¹ band to 1590 cm⁻¹ and an increase in the ratio of the intensities of the 1360 cm⁻¹ to the 1590 cm⁻¹ as compared to perfect graphite. These changes in the Raman spectra imply a change in the graphite structure as a result of the presence of boron in the lattice. T-300 carbon fibers coated with BCx have superior oxidation resistance as compared to uncoated fibers.

Carbon-carbon (C-C) composites are of great importance to the aerospace industry as a thermostructural material. Development of carbon/carbon materials began in 1958, and was supported early on by the U.S. Air Force Dyna-Soar space plane program and the NASA Apollo projects. With the advent of the space shuttle program came intensified research in the area of C-C composites. The impetus behind studying structural carbon composites is the need for materials which have higher specific strength than conventional aluminum, titanium and nickel based alloys, and can withstand higher use temperatures. Of critical importance is the type of fiber used as the reinforcement in these composites.

The specific tensile strengths of several candidate high temperature structural fibers are plotted as a function of temperature in Figure 1. Clearly, the carbon fiber has a higher specific strength than the other fibers. Perhaps more importantly, in an inert environment, the carbon fiber shows virtually no degradation in specific strength as the temperature is increased in excess of 1800°C. Because of these superior mechanical properties, carbon fiber is used as the reinforcement phase in C-C composites. These composites have in turn been used as a thermostructural material in rocket nozzles, airplane brakes, and in the nose cap and leading edges of the space shuttle. These composites are also a candidate material for the mechanically attached thermal protection system of the proposed National Aerospace Plane (NASP). The problem with using carbon for such applications is that it oxidizes at temperatures in excess of 400°C. A possible solution to this problem is the use of BCx as an oxidation resistant alternative to C-C structural materials.

BCx 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. The reaction of interest for the synthesis of BCx is the vapor deposition reaction at 700°C to 800°C between BCl3 benzene to produce a solid boron-carbon film and hydrogen chloride gas, as shown in Figure 2. Under these conditions, a Friedel (continued, page 2)
Novel Compound BC\textsubscript{X} (continued)

Crafts-like reaction occurs. Benzene rings are linked by boron atoms depositing a hexagonal BC\textsubscript{X} structure.

The chemical composition of BC\textsubscript{X} was established by combusting the compound in fluorine to give BF\textsubscript{3} and CF\textsubscript{4}. The relative ratio of these gases was determined by IR absorption spectrometry, which indicated a C:B ratio of 3:1. This ratio of carbon to boron was also determined from electron energy loss spectra. Feecko, Jones, and Thrower determined the concentration of boron in their BC\textsubscript{X} films to be on the order of 20\% via arc emission spectroscopy. However, our analysis of the arc emission spectra revealed the concentration of boron in the BC\textsubscript{X} films to be closer to 15\%.

Finally, recently reported Scanning Auger microscopy results indicate that the maximum amount of boron incorporated in the BC\textsubscript{X} structure is 17\%. This is the boron concentration that would exist in BC\textsubscript{5}.

The published literature on this subject supports a graphite-like structure with boron incorporated into the lattice. Presently, the structure of BC\textsubscript{X} is being modeled at Alfred University. This structure contains ~15\% boron distributed symmetrically in a graphite lattice.

The reaction furnace consists of a clamshell furnace, mass flow controllers, standard roughing pump, and activated carbon and soda-lime filters. The reactant gases were 99.9\% purity BCl\textsubscript{3} and Fisher Scientific, Spectranalyzed C\textsubscript{6}H\textsubscript{6}. The carrier gas was ultra high purity helium.

The BC\textsubscript{X} films were deposited onto fused silica slides, as well as T-300 PAN carbon fibers. Two substrates were used to characterize the BC\textsubscript{X} films. The BC\textsubscript{X} film has a dark metallic mirror-like appearance. The film appears to have a relatively homogeneous morphology. The composition of the BC\textsubscript{X} films produced during the current study was investigated through the use of Secondary Ion Mass Spectroscopy (SIMS). These films contain a significant amount of boron and carbon. Work continues to establish the exact boron concentration.

The structure of the BC\textsubscript{X} films were studied primarily by XRD, electron diffraction and Raman spectroscopy. The XRD diffraction patterns for SP-1 graphite and a BC\textsubscript{X} film are compared in Figure 3. These diffraction patterns strongly support the theory that BC\textsubscript{X} has a structure similar to graphite. The measured \(d_{002}\)-spacing for BC\textsubscript{X} was 0.3353 nm. The \(d_{002}\)-spacing for SP-1 graphite was 0.3348 nm. Substitutionally doping thermos-structural carbons with up to 2.3 at.\% boron results in contraction of the graphite basal plane (lowers the \(d_{002}\)-spacing). It has also been shown in BC\textsubscript{X} films that \(d_{002}\)-spacing decreases to approach that of perfect graphite as boron concentration is increased to 17 at.\%. Furthermore, there is a tendency for the oxidation rate of T-300 carbon fibers coated with these BC\textsubscript{X} films to decrease. The oxidation resistance of the BC\textsubscript{X} coating increases with decreasing \(d_{002}\)-spacing. All four of the \(d\)-spacings that could be determined from the electron diffraction pattern of BC\textsubscript{X} matched the graphite diffraction pattern given by JCPDS card number 41-1487.

The Raman spectra of a BC\textsubscript{X} film is displayed in Figure 4. Raman peaks appear at 1360 cm\textsuperscript{-1} and 1590 cm\textsuperscript{-1}. As-received, polycrystalline graphites exhibit Raman bands at 1360 cm\textsuperscript{-1} and 1575 cm\textsuperscript{-1}. The 1575 cm\textsuperscript{-1} band has been attributed to an E\textsubscript{2g} mode involving vibrations within the graphite layer planes. The 1360 cm\textsuperscript{-1} band is associated with a decrease in crystallite size, and an increase in unorganized carbon in polycrystalline graphite. The shift of the 1575 cm\textsuperscript{-1} band to 1590 cm\textsuperscript{-1} indicates a change in vibrational frequency that results from the addition of boron into the lattice structure of graphite as a substitutional impurity. The mechanism responsible for this shift has not yet been clarified.

The intensity ratio of the 1360 cm\textsuperscript{-1} band to the 1575 cm\textsuperscript{-1} band has been used as a measure of the relative concentration of lattice defects present in the graphite structure. Since disordered carbons are more susceptible to oxidation than well ordered carbons, it is proposed that Raman data (the intensity ratio of the 1360 cm\textsuperscript{-1} band to the 1575 cm\textsuperscript{-1}) can be used to predict the relative oxidation resistance of various carbon forms, which include novel carbon forms such as BC\textsubscript{X}.

Results of Thermal Gravimetric Analysis (TGA) of both as-received T-300 carbon fiber and T-300 carbon fibers coated with BC\textsubscript{X} are shown in Figure 5. In all cases these specimen were exposed to ultra-high purity O\textsubscript{2}, flowing at 20 cm\textsuperscript{3}/min at 600°C. The weight loss curves shown in Figure 5 are broken down into three distinct, steady-state regions. It is apparent that only the T-300 carbon fiber coated with a well-ordered BC\textsubscript{X} film (\(d_{002}\)-spacing = 0.3353 nm) exhibits an initial slow oxidation rate (Region I). More rapid oxidation (Region II) occurred in all three cases, and a region of virtually no oxidation (Region III) occurred only where the fibers were coated with BC\textsubscript{X}. These results imply that only the well ordered BC\textsubscript{X} film offers significant oxidation protection. In uncoated T-300 carbon fibers there was no residual material. For fibers coated with the well ordered BC\textsubscript{X} film, the residual material was BC\textsubscript{X} shells, completely devoid of any evidence of glass, as shown in Figure 6.

There are three possible mechanisms by which the presence of boron can
Novel Compound BC$_X$, (continued)

inhibit carbon oxidation. Boron can act as an electron acceptor, which results in lowering of the Fermi level of the graphite host material. This electron transfer was found to be responsible for oxidation inhibition of carbon fibers doped with low (<200 ppm) boron levels, as observed by a large increase in the activation energy for the O$_2$-Carbon fiber reaction. A second oxidation inhibition mechanism is associated with ordering the graphite structure as a result of boron’s presence. As the structure becomes more ordered, the number of active surface sites decreases. The third mechanism is attributed to exposed boron that reacts with O$_2$ to form B$_2$O$_3$ glass at specific active surface sites. This glass acts as a physical barrier to oxidation, thereby, protecting the host material.

No glassy material is apparent in the well-ordered BC$_X$ shells, which rules out the physical barrier protection mechanism for this class of film. It is the influence of boron on the ordering of the BC$_X$ layer planes that has the dominant effect on oxidation resistance.

CVD films of hexagonal boron rich carbon were deposited from benzene and boron trichloride at 725°C. The d$_{002}$- spacings of these materials are close to that of perfect graphite, and the electron diffraction pattern is similar to that of graphite, which strongly supports the hypothesis that BC$_X$ has a graphite-like structure. The Raman spectra of BC$_X$ revealed that the 1575 cm$^{-1}$ band associated with graphite was shifted to 1590 cm$^{-1}$. This shift indicates a change in vibrational frequency as a result of the addition of boron substitutionally into the graphite lattice. T-300 carbon fibers coated with a well ordered BC$_X$ film have better oxidation resistance than uncoated fibers. The less-ordered films offer considerably less protection. The less-ordered films produce what is suspected to be B$_2$O$_3$ glass during oxidation. There was no evidence of glass formation in the well-ordered BC$_X$ films, indicating that the dominant oxidation protection mechanism for such films was the high degree of ordering between graphitic BC$_X$ layer planes.

Charlie Hach is a Ph.D. candidate in Dr. Linda E. Jones’ research group at Alfred University. On-going laboratory studies include the high-temperature oxidation of C-C components and the use of porous ceramics for emissions abatement. Please contact authors for further references regarding this article.

Combustion Synthesis, (continued)

by Krätschmer and Huffman: carbon vaporization using an electric arc discharge between two graphite rods. The arc method is simple, relatively cheap, and produces high fullerene yields (ca. 10%) from the vaporized carbon which is collected. At present the world-wide demand for fullerenes is made up totally of research laboratories using small quantities. However, what if the results of these laboratory experiments generate useful fullerene-derived products and demand changes from kilograms per year to tons per day? What then would be the most desirable method of producing large amounts, even commodity chemical amounts, of fullerenes?

When we examine the arc process in light of scale-up concerns, we see it has a number of deficiencies. First, it is inherently a batch operation. The rods are loaded, “burned,” and the vaporized dust is collected for fullerene extraction. For scale-up we would desire a continuous process. Second, the electrical input to the arc is a costly method of generating heat. Finally, the cost of the carbon used in the rods is high. Combustion synthesis of fullerenes is a continuous process that we have been investigating, which can address these constraints.

The initial discovery of fullerene synthesis in flames was made by Gerhardt and coworkers of Homann’s group in Germany in 1987. These investigators observed C$_{60}$ and C$_{70}$ ions in low-pressure, sooting flames of benzene and acetylene. Although fullerenes were present, only relatively low ion concentrations were measured. The total amount of fullerenes produced was unknown. Later, McKinnon and Howard at MIT extracted soot samples from low pressure benzene flames using toluene and determined that relatively large amounts of fullerenes are formed. The soot samples contain up to about 15% by weight as fullerenes, mostly C$_{60}$ and C$_{70}$. Not all the fuel carbon is converted to soot. On a basis of fuel carbon, as much as 1% of the mass is in the form of fullerenes. Most experiments have concentrated on using well characterized simple fuels such as benzene and acetylene. One of the keys to cheaply producing fullerenes is to substitute high cost feedstocks with low-value materials such as petroleum residuum.

Thermodynamic analyses predict that the optimum conditions for fullerene synthesis are at very low pressures and very high temperatures. All experimental evidence supports the theoretical predictions. The experiments run in the range of

(continued, page 4)
Combustion Synthesis, (continued)

15 to 75 torr. Theory also predicts that we will continue to increase fullerene yields if we could push the flame temperature beyond the adiabatic limit. One goal is to optimize the pressing conditions to produce the greatest fullerene yields.

Figure 1 shows a surface plot of experimental fullerene yields (surface is a fit to data) as a function of pressure and equivalence ratio (a normalized fuel-air ratio). As the figure shows, equivalence ratio has a tremendous effect on yield and pressure is somewhat less so. A third process variable, held constant in this figure, is inlet gas velocity. Fullerene yields increase monotonically with gas velocity.

A second, and more ambitious goal, is to unravel the complicated mechanisms by which fullerenes form in flames. We normally consider combustion a process in which fuel molecules are broken down into smaller oxidized molecules like CO₂ and water. However, fullerene formation clearly involves molecular weight growth. We can look to a related process in flames for guidance — soot formation.

While the mechanisms of soot nucleation and growth are by no means totally understood, combustion scientists believe that the process is dominated by the addition of small C₃ units (generally believed to be acetylene) to larger aromatic ring networks known as PAH (poly-cyclic aromatic hydrocarbons). The addition occurs at a free radical site on the PAH. Work on soot nucleation has indicated that the sequential addition of acetylene to PAH probably is not fast enough to form soot nuclei as rapidly as they are observed to form in flames. A second process, reactive coagulation, is likely to be important. Reactive coagulation is the linking of two PAH structures at their radical sites to form a larger molecule. In this way, large molecules and soot nuclei can be rapidly assembled. Numerical modeling of sooting flames, using reasonable (but estimated) rate constants, indicates that these processes can account for the observed rates of soot nucleation.

Our working hypothesis is that the same processes which are operative in soot nucleation are also important for fullerene formation in flames. Because soot formation almost always accompanies fullerene synthesis, the assumption that the processes are related appears not to be unreasonable. However, there is one important difference between soot and fullerenes. Soot nuclei can be considered a large molecule with an undefined structure and stoichiometry; we only define the lower limit of the molecular weight. Fullerenes, of course, have a well defined structure, stoichiometry, and molecular weight. Thus, the fullerene mechanism must include processes in which the growing fragment gradually assumes a spherical shell structure with all the peripheral hydrogens eliminated.

The spherical nature of fullerenes is introduced through the inclusion of five-membered rings in the six-membered networks. Thus, the pre-fullerene fragments should include five-membered rings as well. It is unlikely that the process of growth through acetylene addition will lead to an aromatic network which has all the five-membered rings in the correct location. The random nature of the free radical addition process argues strongly against such a directed growth process. To make a fullerene-like network, a mechanism is needed to isomerize a PAH molecule into one which has every five-membered ring in the correct location. Scott and Roeof in 1989. He has been at CSM as an assistant professor since 1991 doing research in applied combustion chemistry.

Figure 1. A surface plot showing the effect of equivalence ratio (normalized fuel/air ratio) and pressure on the fullerene yield. Fullerene yield is defined as (mass of C₆₀ + C₇₀)/mass of soot collected.

In summary, novel production methods based on combustion exist which hold the possibility of greatly reducing the costs of producing fullerenes on a large scale. Besides the normal fullerenes, tubular carbon structures are also produced in the gas-phase environment. An investigation into the mechanisms of fullerene formation indicates that a process similar to soot formation can account for observed production rates. However, additional isomerization steps are required.

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Recycled Plastics as an Energy Source
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POTENTIAL FOR RECOVERED ENERGY

Polymers, long chain molecules often having carbon atoms along their backbone, have displaced a number of metals and ceramics since their commercial introduction over one hundred years ago. The high volume commodity polymers are built from monomers based on natural gas and petroleum, and represent these fuels stored in solid form. The displacement of metals, wood, and ceramics by plastics has occurred because plastics have high strength per unit weight. About 88% of the plastics used in the U.S. are based on only fourteen resins. Each of these resins has different chemical, mechanical, and combustion properties.

Size of the Solid Waste Problem
As the volume of plastics has increased for industrial and consumer use, the interest in recycling plastics for their material and energy value has increased as well. In 1960, about 450 million kilograms of plastics were produced in the United States. By 1984, the U.S. production was 700 million kg, and it is expected to double by the year 2000. Thirty-one billion pounds per year represents a significant solid material resource, and, at bulk densities typically 40 lb/ft³ or less, a significant solid waste issue — if the major method for disposing of used plastics is the landfill. In addition to their low bulk densities, commodity polymers chemically degrade at very, very low rates in the absence of oxygen and light. In fact, landfill burial of plastics is probably a good way of preserving them.

Sources of Waste Plastics
There is not much opportunity for identifying large waste streams for recycling from industrial sources. Fabrication of parts and assemblies results in 25 to 40% unused material per cycle, and most of this plastic is regrinded, reprocessed, or used in other ways.

Post-application recycling, the reuse of plastics after their normal service life, has received much attention in the United States over the past ten years. Plastic use can be divided into five major categories: packaging, durable goods, transportation, electrical, and construction. The focus has been on consumer articles, such as plastic bottles, plastic film, and foamed packing materials, because the volume and impact of these materials are obvious to everyone. According to the Society of the Plastics Industry, about 31% of the plastics usage in 1984 was for packaging (11 billion pounds). Packaging applications have lifetimes of less than one year, so that essentially all of this material becomes waste shortly after it is produced. The technical difficulties of recycling packaging include collection of this dispersed resource, transportation to a central site for processing, and, for most recycling applications, separation of the plastics by chemical type.

Durable goods and transportation applications use 6% of all plastics produced; electrical uses 7%; and construction uses 25%. However, these applications are characterized by much longer lifetimes: 5 years for transportation; 10 years for durable goods and electrical; and as much as 50 years for building and construction. The use of plastics in these applications has accelerated over the last ten years, so we should expect large volumes of solids to be available in the future.

The size of the plastics stream going into the construction industry is large, and it has long usage lifetime. Plastics are used as siding, insulation, flooring, carpeting, as well as in furniture and fixtures. Lifetimes range from 20 to 50 years, so that this material stream will become significant only as old homes are torn down and new ones are built. Buildings can be regarded as warehouses for recyclable plastics because the mass used in this application equals that used in packaging.

Example: Recycling Automotive Plastics.
Recycling of automotive plastics is an interesting case in point. In the late 1980’s, there were about 200 lb of plastics used per automobile, and this amount may be increasing to the 400-500 lb/car level in the near future. Since the lifetime of an automobile is over 5 years, there will be a lag time before this material becomes solid waste. For example, the plastics put into cars today will be available for collection at an automotive dismantler after we enter the 21st century. Automobile manufacturers are aware of the environmental impact of this large material stream, and are starting to address the disposal issues. BMW has plans to take back entire cars at the end of their service and recycle everything. There are research and demonstration plants for recycling and combusting tires, automotive shredder waste, SMC (sheet molding compound used for exterior body parts), and other plastics.

While this resource is smaller in size and more diverse chemically, it has one distinct advantage over packaging waste. There are about 12,000 automotive dismantlers in the U.S. as compared to millions of households. This low number of collection points should keep recycling costs low by reduced transportation distance after collection, higher bulk density of transported waste after chipping of the plastics at the dismantler, and the possibility for the separation of recycled plastics by chemical type. Macrosorting, separation as whole parts, would be the first step in producing purified, recycled polymers. Automated macrosorting of plastic bottles has been demonstrated to be over 90% accurate, and could be implemented at high volume dismantlers. Bumpers, taillights, and dashboards might be removed, chipped and stored in bins for pick-up and transport. Microsorting, separation of chipped material by physical or chemical property differences, can be used to purify the material further.

Impact of Plastics-to-Energy Conversions
The amount of energy available for recovery from waste plastic materials is large. In 1988, about 3% of the total U.S. energy consumption went to the production of plastics. Half of this energy represents the fuel value of the petroleum and natural gas used as the raw materials.
Commentary, (continued)

The remainder was used to process the feedstocks, and to transport intermediates and finished products. One-third of the processing energy came from coal, hydropower and nuclear energy sources.

Both post-consumer recycling and plastics-to-energy conversion would reduce the amount of natural gas, petroleum, and other energy sources used to make plastics. Recycling reduces the raw materials needed. Plastics-to-energy conversion recovers the fuel value for other needs. Each method reduces the impact of solid plastic waste on landfills. Other countries (Japan, Taiwan and Germany) with less landfill capacity are ahead of us, and already recycle high percentages of their plastic waste to material and energy uses.

Solid plastic waste represents a significant stream for conversion back to energy. The typical heat of combustion for the monomers of commodity polymers is 20,000 Btu/lb, so that, by the turn of the century, there will be over 600 quads (1012 Btu) per year of energy available from the plastics produced in the U.S. Technologies for accomplishing this conversion may vary by the source of the plastic, and its typical composition. These issues will be discussed in the next issue of Energeia.