Radiation Shielding Materials Containing Hydrogen, Boron, and Nitrogen: Systematic Computational and Experimental Study - Phase I

NIAC FINAL REPORT

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Abstract

The key objectives of this study are to investigate, both computationally and experimentally, which forms, compositions, and layerings of hydrogen, boron, and nitrogen containing materials will offer the greatest shielding in the most structurally robust combination against galactic cosmic radiation (GCR), secondary neutrons, and solar energetic particles (SEP). The objectives and expected significance of this research are to develop a space radiation shielding materials system that has high efficacy for shielding radiation and that also has high strength for load bearing primary structures. Such a materials system does not yet exist. The boron nitride nanotube (BNNT) can theoretically be processed into structural BNNT and used for load bearing structures. Furthermore, the BNNT can be incorporated into high hydrogen polymers and the combination used as matrix reinforcement for structural composites. BNNT’s molecular structure is attractive for hydrogen storage and hydrogenation.

There are two methods or techniques for introducing hydrogen into BNNT: (1) hydrogen storage in BNNT, and (2) hydrogenation of BNNT (hydrogenated BNNT). In the hydrogen storage method, nanotubes are favored to store hydrogen over particles and sheets because they have much larger surface areas and higher hydrogen binding energy. The carbon nanotube (CNT) and BNNT have been studied as potentially outstanding hydrogen storage materials since 1997. Our study of hydrogen storage in BNNT - as a function of temperature, pressure, and hydrogen gas concentration - will be performed with a hydrogen storage chamber equipped with a hydrogen generator. The second method of introducing hydrogen into BNNT is hydrogenation of BNNT, where hydrogen is covalently bonded onto boron, nitrogen, or both. Hydrogenation of BN and BNNT has been studied theoretically. Hyper-hydrogenated BNNT has been theoretically predicted with hydrogen coverage up to 100% of the individual atoms. This is a higher hydrogen content than possible with hydrogen storage; however, a systematic experimental hydrogenation study has not been reported. A combination of the two approaches may be explored to provide yet higher hydrogen content. The hydrogen containing BNNT produced in our study will be characterized for hydrogen content and thermal stability in simulated space service environments. These new materials systems will be tested for their radiation shielding effectiveness against high energy protons and high energy heavy ions at the HIMAC facility in Japan, or a comparable facility. These high energy particles simulate exposure to SEP and GCR environments. They will also be tested in the LaRC Neutron Exposure Laboratory for their neutron shielding effectiveness, an attribute that determines their capability to shield against the secondary neutrons found inside structures and on lunar and planetary surfaces.

The potential significance is to produce a radiation protection enabling technology for future exploration missions. Crew on deep space human exploration missions greater than approximately 90 days cannot remain below current crew Permissible Exposure Limits without shielding and/or biological countermeasures. The intent of this research is to bring the Agency closer to extending space missions beyond the 90-day limit, with 1 year as a long-term goal. We are advocating a systems solution with a structural materials component. Our intent is to develop the best materials system for that materials component. In this Phase I study, we have shown, computationally, that hydrogen containing BNNT is effective for shielding against GCR, SEP, and neutrons over a wide range of energies. This is why we are focusing on hydrogen containing BNNT as an innovative advanced concept. In our future work, we plan to demonstrate, experimentally, that hydrogen, boron, and nitrogen based materials can provide mechanically...
Introduction

The space environment contains major hazards to space travel, among which are space radiation and micrometeoroid and orbital debris (MMOD). The space radiation consists mainly of electrons and protons, solar energetic particles (SEP), and galactic cosmic radiation (GCR). The GCR is composed primarily of nuclei (fully ionized atoms) plus a small contribution (~2%) from electrons and positrons. There is a small but significant component of GCR particles with high atomic number (Z > 10) and high energy (E > 100 GeV) (Ref. 1). These high energy, high charge (HZE) particles comprise only 1% to 2% of the total GCR fluence, but they interact with very high specific ionizations and thus contribute about 50% of the long-term space radiation dose in humans (Ref. 2). The GCR particles, which are positively charged, interact with materials mainly by Coulomb interactions with the negative electrons and positive nuclei in the materials and to a much smaller extent by collisions with atomic nuclei in the materials. For these reasons, the energy loss of the GCR particles increases approximately with the charge-to-mass ratio of the materials. Hydrogen, with the highest charge-to-mass ratio of any element, provides the best shielding (Ref. 3). Since a shield of pure hydrogen is not practicable, hydrogen containing polymers make the most suitable candidates for shielding. Additional radiation hazards come from neutrons and gamma rays produced in nuclear collisions and from x-rays arising after Coulomb interactions. Neutrons are present inside the space structures; these are produced as secondaries when the space radiation interacts with the walls of the structures. Secondary neutrons are also present on the surfaces of Moon and Mars.

The objectives and expected significance of the proposed research are to develop a space radiation shielding materials system that has high efficacy for shielding all radiations and that also has high strength for load bearing primary structures. Such a materials system does not yet exist.

We know that hydrogen is effective at (1) fragmenting heavy ions such as are found in galactic cosmic radiation (GCR), (2) stopping protons such as are found in solar particle events (SPE), and (3) slowing down neutrons such as are formed as secondaries when the GCR and SPE interact with matter. Hydrogen, however, by itself is not a structural material. Polyethylene, with its empirical formula of CH₂, contains a lot of hydrogen and is a solid material, but it does not possess sufficient strength for load bearing aerospace structural applications. The industry appears to be stuck with aluminum alloys for primary structures, retrofitted with polyethylene or water (H₂O) for radiation shielding. Clearly, a newer paradigm or concept is needed.

The NASA Langley Research Center (LaRC), Jefferson Sciences Association (JSA), and National Institute of Aerospace (NIA), as joint owners, have recently synthesized long, highly crystalline boron nitride nanotubes (BNNT) using a novel pressure/vapor condensation method. The BNNT have extraordinary strength and high temperature stability. The BNNT are made up entirely of low Z (atomic number) atoms - boron and nitrogen. Boron (Z=5) and nitrogen (Z=7) are larger than hydrogen (Z=1), but they are still small and they are smaller than aluminum (Z=13).

The BNNT can theoretically be processed into structural BNNT, which is thermally stable up to 800°C in air, and used for load bearing structures. Furthermore, the BNNT are molecules; they can be incorporated into high hydrogen polymers and the combination used as
matrix resins for structural composites. The BNNT are nanotubes; their molecular structure is attractive for hydrogen storage.

Boron has one of the largest neutron absorption cross sections of all the elements of the periodic table, and nitrogen has a larger neutron absorption cross section than carbon. The neutron absorption cross section for the isotope B\(^{10}\) is 3835 barns, so enriching the BNNT or BN (boron nitride) with B\(^{10}\) would produce even better protection against neutrons.

Neutrons are produced as secondary radiation when the GCR and solar energetic particles (SEP) interact with the walls of the space structure (vehicle, lander, habitat) and also with the regolith on the surface of Moon or planets. This secondary neutron radiation has largely been ignored in previous space architectures, and yet neutron radiation is known to be damaging to humans especially with regard to the formation of radiogenic cancers.

The possibilities are immense for using BNNT for multifunctional radiation shielding structural materials for future space exploration architectures. This early study is focused on a visionary aerospace concept. This is an architecture or systems concept, currently at TRL = 1-2 in maturity, aiming 10 or more years in the future. This is a truly revolutionary concept that could redefine the future possibilities for NASA.

**Computations**

During the Phase I research, numerous materials were modeled for their effectiveness at shielding galactic cosmic radiation (GCR) and solar energetic particles (SEP). The computer code used was OLTARIS (On-Line Tool for the Assessment of Radiation in Space) (Ref. 4). OLTARIS is an integrated tool set utilizing the HZETRN (High Charge and Energy Transport) code developed at the NASA Langley Research Center. These tools are intended to help scientists and engineers study the effects of space radiation on shielding materials, electronics, and biological systems.

The results of our modeling study showed that the higher the hydrogen content of the material, the better the radiation shielding effectiveness against both GCR and SEP. Water contains hydrogen, but it is a liquid and not a structural material; it can be used as part of the total radiation shielding system because water is a necessary consumable for all human exploration missions. Polyethylene is a solid material, but it does not have the strength and thermal stability to be a structural material for space applications. It also has some outgassing and flammability issues and should be encapsulated for many applications.

How then can we produce a structural material that has high hydrogen content? We believe the answer is in BNNT. The structural properties are already verified. Suppose we could use the BNNT as the “vehicle” for carrying more hydrogen into the system. BNNT has the molecular nanotube structure and has a density of 1.3 - 1.4 g/cm\(^3\). It can hold a lot of hydrogen!

Our OLTARIS modeling study indicates that hydrogen containing BNNT may offer excellent shielding effectiveness against GCR and SEP. When wall thicknesses and forms of materials that could actually be used to build spacecraft are considered, BN materials perform better than liquid hydrogen (LH\(_2\)) and water. BN + 5% H performs better than state-of-the-art polyethylene as seen in Figure 1, where each material is 30-cm thick.
Each material is 30-cm thick.

Figure 1. Calculated exposure to galactic cosmic radiation (GCR) with shielding by a wall of the same thickness (30 cm) made of various materials.

Figures 2 and 3 show our calculated results for GCR dose equivalent and SPE dose equivalent, respectively, for BN plus varying weight percents of hydrogen, as functions of areal density (g/cm$^2$). In both of these figures, one sees that liquid hydrogen LH$_2$ is the best shield, but one cannot build structures out of liquid hydrogen. The next best shield in both figures is the BN + 20% hydrogen. This is a solid material, and it can be used for structures.
Figure 2. Galactic cosmic radiation (GCR) dose equivalent for BN + H materials.
Figure 3. Solar particle event (SPE) dose equivalent for BN + H materials.

From our Phase I research, we have learned the following:

- BNNT outperforms current SOA (state-of-the-art) structural materials from a mechanical and thermal perspective.
- BNNT alone does not outperform current SOA radiation shielding materials - except for the case of secondary neutrons.
- 5% (by weight) hydrogen containing BNNT does outperform current SOA radiation shielding materials of the same linear thickness, with the increase in protection being substantial.
- Several of the key technical challenges for BNNT relate to production (increased yield, scalability, and the capability to grow even longer tubes). LaRC is now producing tubes again (after relocating the equipment from one facility to another). The work on BNNT production is funded from a different program source, and so we were able to leverage off this other funding for our NIAC work. This allowed us to focus on radiation shielding.
- The major radiation protection challenge for human spaceflight is against GCR. SEP and secondary neutrons are also significant challenges, and BNNT can serve as a significantly enhancing solution to these. The team has realized that our focus should be on exploring
the requirements and needs for a GCR solution, because BNNT can likely provide either an enabling or significantly enhancing GCR solution, with the understanding that the system thus produced will also provide solutions to the SEP and neutron challenges.

- We have identified the rationale to explore the hydrogen containing BNNT approach for protection against GCR radiation.

Processing of BN/Polymer Nanocomposites

The primary objective for our processing work for the Phase I was to process polyimide composite films of varying weight percents of hexagonal boron nitride (h-BN). Some of the initial films that were made were then tested for tensile strength, hardness, toughness, and glass transition temperature (Tg). The remaining films will be utilized in making a 0.5 g/cm² layered specimen for neutron radiation exposure analysis to be conducted at LaRC.

LaRC-SI (soluble imide) is a thermoplastic co-polymer. It was selected for this study due to its high strength and thermal durability, as well as its capacity to be processed into thicker structures, not just films. Additionally, LaRC-SI is commercially available in many forms in large quantities. Since it is a soluble imide, it can be purchased not only as a powder, film, or other solid, but also as a solution, something that can offer many simplistic processing techniques for its use in composites. LaRC-SI also contains hydrogen, although not as high a percentage content as polyethylene. Compared with polyethylene, though, it offers much higher mechanical, thermal, and structural properties. Considering all this, LaRC-SI was deemed an excellent choice as the polyimide matrix for the processing of the boron nitride nanocomposites for this study. The molecular structure of LaRC-SI is shown in Figure 4, and some of the properties of LaRC-SI are given in Table I.

![Molecular structure of LaRC-SI](image)

**Figure 4. Structure of LaRC-SI co-polymer polyimide.**

<table>
<thead>
<tr>
<th>Company</th>
<th>Type</th>
<th>Tg (°C)</th>
<th>Cure temp. (°C)</th>
<th>Upper use temp. (°C)</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (GPa)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imitec, Inc.</td>
<td>20% solids solution with 0.5% offset</td>
<td>251</td>
<td>300</td>
<td>230</td>
<td>141</td>
<td>4</td>
<td>1.37</td>
</tr>
</tbody>
</table>

**Table I. LaRC-SI polyimide.**
Hexagonal boron nitride (h-BN) is a structural analog to graphite. It can also be purchased in many forms at a commercial level, including powders, platelets, and ceramics. The powder form of this compound was selected for use in this study for multiple reasons. To start, the use of hexagonal boron nitride (h-BN) allowed for a baseline study comparison for the eventual incorporation of boron nitride nanotubes (BNNT) into polyimide nanocomposites. Hexagonal BN is a composition analog to BNNT, but BNNT offers much more impressive physical properties due to the advanced nanostructure. For example, it is estimated that BNNT has a maximum service temperature of 800°C and a Young’s modulus of 1.18 TPa. It is expected that the addition of BNNT to composites will greatly improve the material’s strength and thermal resistance, among other properties. Additionally, h-BN was selected for this study since boron has one of the largest thermal neutron capture cross sections among the periodic elements. Borated polyethylene is in fact used commercially as a radiation shielding material. The high hydrogen content of the polyethylene is good at slowing down the incident radiation to lower energies, such as within the thermal energy region, and then the boron is able to absorb the low energy radiation. Together the composite works as a great shielding system. Additionally, h-BN was selected for use in this study since it also has some wear-resistance properties due to its graphite-like structure. The powder form of the material was selected, as it provided the easiest means of incorporating the h-BN into polyimide nanocomposites. Figure 5 shows the structure of hexagonal boron nitride (h-BN), and Table II gives some of the properties of h-BN.

![Hexagonal boron nitride structure](image)

**Figure 5. Structure of h-BN.**

<table>
<thead>
<tr>
<th>Company</th>
<th>Grade</th>
<th>Particle size (µm)</th>
<th>Surface area (m²/g)</th>
<th>Tap density (g/cm³)</th>
<th>Apparent density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saint-Gobain</td>
<td>PSHP</td>
<td>6</td>
<td>7</td>
<td>0.35</td>
<td>2.2</td>
</tr>
<tr>
<td>Momentive Performance</td>
<td>NX1</td>
<td>0.8</td>
<td>20</td>
<td>0.12</td>
<td>2.2</td>
</tr>
<tr>
<td>Materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The solvent used in the processing was N-methylpyrrolidone (NMP), which is an organic solvent. Figure 6 shows the molecular structure of NMP, and Table III gives some additional information for the NMP used in this study.

![Molecular structure of NMP](image)

**Figure 6. Molecular structure of NMP.**

<table>
<thead>
<tr>
<th>Company</th>
<th>Grade</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fisher Biotech</td>
<td>peptide synthesis grade</td>
<td>202-204</td>
</tr>
</tbody>
</table>

A total of forty-three high-quality films were processed for this study, with varying weight percents of h-BN - specifically 0%, 5%, 10%, and 20%. Twenty of the films were reserved for the fabrication of the layered neutron radiation exposure specimen. The average measured thickness of each film was around 0.3-mm thick. The average density of each film with the 10% h-BN was around 1.42 g/cm³. Characterization of these films will be continuing, including neutron exposure testing in LaRC’s 1-Curie americium-beryllium source.

### Technical Work Plan for Hydrogen Containing BNNT

The major focus for the next phase of our research effort is to study the major feasibility issues associated with the cost, performance, development time, and key technologies pertinent to the development of the hydrogen containing BNNT concept for radiation shielding. LaRC is already making high-quality BNNT, so we have a readily available supply of the tubes for our work. Simultaneous with our work on hydrogen containing BNNT, a sizable effort at LaRC is underway on the further development of the BNNT with other program funds. This other work is focused on increased production yield and also on decreased costs for production and purification of the BNNT.

There are two paths for introducing hydrogen into BNNT:

- Hydrogen storage in BNNT
- Hydrogenation of BNNT (hydrogenated BNNT)

The first approach is the hydrogen storage route. A number of studies have been published about hydrogen storage nanostructured materials. Nanotubes have been favored to store hydrogen over particles and sheets because they have more surface area and higher hydrogen binding energy. Carbon nanotubes and boron nitride nanotubes have been studied as
outstanding hydrogen storage materials since 1997 (Ref. 5). Theoretical \textit{ab initio} calculations showed that BNNTs are a preferable medium for hydrogen storage compared with CNTs because of the heteropolar binding nature of their atoms (Ref. 6). BNNT bonds, because of their ionic character, offer 40% higher binding energy of hydrogen than CNT bonds. The point charges on the tube’s wall induce a dipole on the hydrogen molecule resulting in more efficient binding (Ref. 7). The binding energy in BNNTs is even greater than that in planar BN sheet by about 10%, which is presumably due to the buckling (curvature with \textit{sp}^3 nature) of BN bonds. The diffusion of hydrogen is therefore slower in small diameter BN nanotubes than in larger diameter ones (Ref. 8). Therefore, the hydrogen desorption temperature of BNNT is expected to be much higher as well, which is beneficial for use in high temperature environments. Experimentally, multiwall bamboo-like BNNT showed up to 2.6 wt% hydrogen storage (Ref. 9), and collapsed structure BNNTs could store up to 4.2 wt% hydrogen (Ref. 10) even at room temperature, which is significantly higher than for CNTs. The majority (95%) of the adsorbed hydrogen was safely stored up to 300 to 450\textdegree{}C.

The BNNTs produced by NASA LaRC (Ref. 11) may store much higher hydrogen than the reported BNNTs because they can provide much higher specific surface area (SSA) with thinner and longer tubes. They can provide also smaller pores among the bundles, which allows more effective absorption of hydrogen with higher heat of adsorption (Ref. 12).

Figure 7 shows hydrogen storage in different types of nanotube bundles - carbon NTs and boron nitride NTs. The photographs are taken from grand canonical Monte Carlo simulations (modified from Ref. 7).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{hydrogen_storage.png}
\caption{Hydrogen storage in different types of nanotube bundles – carbon NTs (left) and boron nitride NTs (right).}
\end{figure}

Several theoretical studies to improve the hydrogen storage capacity have been published. Defects on the BNNT wall can improve the hydrogen storage. The vacancies reconstruct by forming B-B and N-N bonds across the defect site, and the defects offer smaller charge densities that allow hydrogen molecules to pass through the BNNT wall for storing hydrogen molecules inside the BNNT (Ref. 13). In addition, metal (rhodium, nickel, palladium, or platinum) doped BNNTs can store more hydrogen molecules because hydrogen interacts highly with metal atoms due to the hybridization of the metal \textit{d} orbital with the hydrogen \textit{s} orbital (Ref. 14). The thin, long LaRC BNNTs possess well-defined inner tube storage to take up hydrogen more effectively.
compared with bamboo or herringbone type BNNTs. Nitric acid treatment can open the tips of the tubes and create minor defects to expedite hydrogen uptake into the tubes also.

Our study of hydrogen storage in LaRC BNNTs will be performed - as a function of temperature, pressure, and hydrogen gas concentration - with a hydrogen storage chamber equipped with a hydrogen generator. A quartz hydrogen chamber (Carbolite, Ltd.) and a pressure chamber (5100 Reactor, Parr Instrument Company) will be used, both of which are already available in our laboratory (Fig. 8). The uptake hydrogen content will be analyzed with a modified surface analyzer (Nova 2200e, Quantachrome) and TGA-mass spectroscope (STA 409, Netsch).

The second approach is the hydrogenation of BNNTs, with hydrogen bonded covalently onto boron or nitrogen or both. The hydrogenation of BN and BNNT has been studied theoretically (Refs. 13 and 15). Hyper-hydrogenated BNNTs can be created with hydrogen coverage up to 100% of the individual atoms, theoretically. Therefore, higher hydrogen content can be achieved by this approach compared with the hydrogen storage approach; however, a systematic experimental hydrogenation study has not been reported. Although high hydrogen containing BNNTs can be achieved, this approach may sacrifice to a certain extent the other attractive structural and thermal characteristics of BNNTs by disrupting $p$ conjugated $sp^2$ BN bonding. An optimum degree of hydrogenation should, therefore, be determined depending on the missions to be applied.

A hydrogen plasma quartz chamber and a low-pressure hydrogenation chamber with a catalyst will be employed for hydrogenation. Raman, FTIR, and TGA-mass spectroscopy will be used to assess the degree of hydrogenation.

Combining both hydrogen storage and hydrogenation approaches may provide synergistically improved radiation shielding effectiveness because modified $sp^2$ bonds on BNNTs can afford more hydrogen storage. We shall try both approaches.

Once we have produced thermally stable high hydrogen containing BNNTs, we shall then incorporate them into high hydrogen, high performance polymers. NASA LaRC has world-class high performance polymer synthesis expertise and facilities, so this shall be the easiest part of our research. The resulting polymeric materials or nanocomposites will be characterized at LaRC for a number of relevant mechanical, dynamic mechanical, and thermal properties for space structural applications.
We shall also characterize the hydrogen containing BNNT composites for their radiation shielding effectiveness. They will be tested in the LaRC Neutron Exposure Laboratory. This facility has a 1-Curie americium-beryllium source and an indium foil detector with a programmable counter. High energy proton and high energy, heavy ion beam testing will also be conducted at outside facilities. Historically, we have conducted our radiation beam testing at the NASA Space Radiation Lab (NSRL) located at the Brookhaven National Lab (BNL), the Lawrence Berkeley National Lab (LBNL), and the HIMAC (Heavy-Ion Medical Accelerator in Chiba) facility in Japan. We plan to continue radiation testing at one or more of these facilities. We shall also continue our OLTARIS radiation transport modeling studies to compare the experimental results with the theoretical predictions.

We intend to explore different forms of our new materials - films, fibers, yarns, fabrics, thick castings, and composites. We intend to explore applications of these forms within the mission concept, protecting humans in crew habitable volumes.

The modeling effort started in Phase I of this work will be continued. Recent and continuing modifications to the OLTARIS (On-Line Tool for the Assessment of Radiation in Space) code are helping to increase the fidelity of this modeling and, in particular, there is ongoing work to better model the effects of radiation on electronics as well as to incorporate the effects of secondary neutrons. As the materials development cycle progresses, there will be an iterative process to determine how the new formulations affect the radiation shielding capabilities as well as give feedback on required changes to the materials. The modeling work will also inform the systems analysis study as well as influence the design of experiments to be conducted at the radiation beam testing facilities. These experiments generally tend to be expensive to set up, conduct, and analyze and, therefore, the modeling work will be essential to maximizing the benefits that can be obtained from them. In addition to calculating the influence of hydrogen on the radiation shielding, there will be a concerted look at the effects that layering different materials has on the radiation environment within the spacecraft. This comes from the appreciation that spacecraft, habitats, and extravehicular activity suits are inherently multilayered structures, as well as the need to look at the possible synergistic shielding effects that different materials layers might have. Among the data that can be obtained from the OLTARIS code are the identities and fluences of the species that result from the interaction of the incoming radiation with the various components of the shield and structure. Using this information and numerical modeling using Genetic Algorithms (GAs), it is intended to further optimize the deployment of materials layers for the most effective shielding. GAs are robust search algorithms that are used in a range of optimization problems and will be used to optimize the sequence of materials that best attenuates the expected secondary particles.

**Pathway to Flight**

As part of the future activities, the team will define a pathway for bridging the “technology valley of death” between the fundamental materials systems technology research and flight, merging the results of the fundamental research, materials systems development, and systems analysis activities into an integrated plan that outlines the remaining challenges and defines a path to flight that overcomes those challenges. Central to the development of this plan will be the mission concept, which will provide a common structure for connecting the bottoms-up research and top-down analysis and serving as a vision for the fundamental research and materials systems development activities and providing context for the systems analysis
activities. This “systems” development approach will focus the team’s energy, ensuring that the research and analysis activities drive the technology towards flight.

The fundamental research activities will develop the approach for getting hydrogen into the BNNTs - through hydrogen storage, hydrogenation, or both - and then processing and characterizing the nanocomposites in different useful forms. This research will retire an existing challenge (identification of an approach for getting hydrogen into the BNNTs), assess the properties and performance of different hydrogen containing forms, and identify any key challenges associated with the initial processing of the hydrogen containing BNNT into various forms. The nanocomposite forms will then be manufactured into materials systems that will be tested on the ground for radiation shielding effectiveness, with the materials system options assessed being aligned to the mission concept. This approach will ensure that the materials system options selection is guided by the initial systems analysis activities, which will focus on characterizing the radiation shielding performance of different materials systems for deep space habitation systems. Insights obtained from manufacturing these materials systems will also be used to inform later systems analysis activities, which will assess the cost and risk impacts of and identify alternative uses for the materials systems.

This integrated approach merges the fundamental research, materials system development, and systems analysis activities together to ensure a complete, systematic, end-to-end assessment that will identify the remaining key challenges - so that a realistic, measured pathway to flight can be laid out for the mission concept, protecting humans in crew habitable volumes.

This investigation into developing a space radiation shielding system using BNNT leverages LaRC’s existing facilities, ongoing research, and licensing agreements. LaRC synthesizes BNNTs using an operational production apparatus consisting of a laser (5-kW CO₂ laser), chiller, pressure vessel, boron feedstock, N₂ gas feed, interlocks, cameras, mirrors, ventilation system (because of the nanoparticles produced), and the appropriate enclosures, blast shields, and utilities for safety and operation. High power laser energy is used to vaporize boron while in a high-pressure nitrogen atmosphere to produce highly crystalline BNNTs. The optimization and scale-up of BNNTs are currently funded research efforts; the resulting data (materials property and composite processing data) can be leveraged at no cost to this radiation study. A suite of BNNT patents has been licensed from NASA and its joint owners. This provides scale-up opportunities for the baseline material and enables the possibility of future large-scale structural components in our roadmap transition plan. LaRC currently has a draft Space Act Agreement in review to work collaboratively with the company that licensed the technology, in order to advance jointly the science and development of BNNT technologies.

A detailed reference mission concept (RMC) will be developed early in this investigation to serve as a common structure for connecting the bottoms-up research and top-down systems analysis. A technology infusion impact assessment will then be performed against this RMC, with a performance-only assessment being developed and a performance, cost, and risk assessment being subsequently developed. To perform the assessment, detailed implementation options for infusing technologies will be developed and then assessed in the context of deep space mission architectures. Mission concepts used for the assessments will include Mars conjunction-, Mars opposition-, 1-year Near Earth Asteroid (NEA), and 2-year NEA class missions.

The pathway to flight definition will be finally developed. The technology- and system-level challenges that need to be resolved before flight will be updated to reflect findings from
earlier study activities. A preliminary pathway to flight will then be iteratively developed by the team that (a) provides a realistic technology development path to flight, (b) defines the technology- and system-level challenges that need to be resolved prior to flight with anticipated retirement paths, (c) identifies the key enabling technologies, their current state of technology readiness, and planned/possible maturation paths, and (d) provides targeted infusion points for Mars, NEA, or lunar architecture being actively considered by HEOMD. An assessment of alternative applications for the technologies will also be provided as part of the pathway to flight, with the common development paths between each alternative application and the mission concept application being identified.

**Concluding Remarks**

During this NIAC Phase I study, we have accomplished the following:

- We have established, computationally, that hydrogen (H) containing BN and BNNT materials (hereby named HBN materials) can outperform the state-of-the-art polyethylene with respect to radiation shielding. Since BNNT materials are vastly superior with respect to mechanical and thermal properties, our HBN materials have the potential to be disruptive, multifunctional, structural radiation shielding materials. This is a Revolutionary Breakthrough!
- We have made a sizable supply of hexagonal boron nitride (h-BN) containing LaRC-SI polyimide nanocomposite films. We have begun characterizing these materials for structural materials properties and radiation shielding effectiveness.
- We have developed a technical work plan using existing LaRC equipment for producing hydrogen containing BNNT (i.e., HBN).
- We have developed a comprehensive computational, experimental, and systems analysis approach for proceeding on a pathway to flight.
References

Biographical Sketches

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Summary of Professional Achievements:
Dr. Sheila A. Thibeault has been a civil servant researcher at NASA LaRC since 1966. Since 1981, she has focused her research on the development of space durable materials and radiation shielding materials systems. From 2006 - 2009, she was the Task Lead for the Radiation Shielding Task, under the Exploration Technology Development Program (ETDP). Her current position is Senior Research Physicist, Advanced Materials and Processing Branch, Research Directorate. She is the author or coauthor of over 200 formal publications and referenceable presentations. She has received many professional awards, including the NASA Exceptional Service Medal in 2000. She is the Langley Principal Investigator (PI) for MISSE 1, 2, 3, 4, 5, 6A, and 6B. Since 2008, she has been the Project PI for MISSE 6A and 6B. She has been the Principal Investigator for the MISSE-X Project since its inception.

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• B.S., Physics, College of William and Mary, Williamsburg, Virginia, 1966.

Selected Professional Awards:
• Superior Accomplishment Award to the Materials International Space Station Experiment (MISSE) Project Team “For Outstanding Dedication and Excellent Performance as a Member of the Materials International Space Station Experiment (MISSE) Project Team,” August 12, 2001.
• NASA Group Achievement Award to the Materials International Space Station Experiment (MISSE) Team “For Outstanding Achievement in the Development, Validation, Launch, and Installation of the MISSE,” August 11, 2003.

Selected Patents and Invention Disclosures:
• Sauti, Godfrey; Park, Cheol; Kang, Jin Ho; Kim, Jae-Woo; Harrison, Joycelyn S.; Smith, Michael W.; Jordan, Kevin C.; Lowther, Sharon E.; Lillehei, Peter T.; and Thibeault,


**Selected Papers and Presentations:**

Dr. Catharine C. Fay  
Co-Investigator  
NASA Langley Research Center  
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Summary of Professional Achievements:  
Dr. Catharine C. Fay is a senior materials engineer at NASA LaRC and currently serves as both the program manager for the Boron Nitride Nanotube (BNNT) Development Team and Assistant Branch Head of the Advanced Materials and Processing Branch. For the BNNT team, she provides technical management for the synthesis, characterization, and application of nanotechnology for aerospace applications. As Assistant Branch Head, Dr. Fay serves as a lead technical expert for materials synthesis, processing, analytical characterization and computational capabilities within the branch. Employed by NASA for nearly 20 years, she has specialized in monomer, polymer, and composite synthesis and characterization for advanced aerospace applications. She served as the Technical Group Leader, Chief Scientist, and Team Lead for materials for the Advanced Aircraft Program specializing in development of new lighter weight materials, integration of new materials into structures, analysis, and coordination with aerospace industry and government partners. She has co-authored 37 technical papers including journal articles, technical memorandums, preprints, and proceedings; articles published in Materials Research Society, AIAA/SDM, SPE and SAMPE proceedings, High Performance Polymers, Journal of Applied Polymer Science, Advanced Performance Materials, and Journal of Plastic Film and Sheeting. Research areas of expertise include polymer synthesis, characterization, nanotechnology, advance aircraft, space transportation, radiation shielding materials, and modeling combined with experimental validation. She is responsible for infusing game-changing and crosscutting technologies throughout the Nation’s space enterprise to transform the Nation’s space mission capabilities by developing a program to scale-up low TRL nanostructured materials, establish purification and assay techniques and evaluate properties (chemical, physical, mechanical, electrical, environmental). Dr. Fay is responsible for development and demonstration of the critical technologies that will make NASA’s exploration, science, and discovery missions more affordable and more capable through research of low TRL nanostructured materials for lighter weight, higher temperature, and more radiation resistant materials which enable more affordable and longer duration missions.

Education:


Selected Professional Awards:

- Post-Doctoral Research Fellow, National Research Council, Laboratory: Langley Research Center, 1996-97.
- AIAA - SDM/Boeing Best Paper Award for "CONSTITUTIVE MODELING OF CROSSLINKED NANOTUBE MATERIALS", 2004.

Selected Patents and Invention Disclosures:

- Kang, Jin Ho; Bryant, Robert G.; Park, Cheol; Sauti, Godfrey; Gibbons, Luke; Lowther, Sharon E.; Thibeault, Sheila A.; and Fay, Catharine C.: Multi-Functional BN-BN Composite. Disclosure of Invention, LAR-18040-1. Provisional application filed.
- Gnoffo, Peter and Fay, Catharine, LAR-18132-1; Modeling of Laser Ablation and Plume Chemistry in a Boron Nitride Nanotube Production Rig, November 2011.

Selected Papers and Presentations:

Ms. Sharon E. Lowther  
Co-Investigator  
NASA  
Langley Research Center, Hampton, VA 23681  
Sharon.e.lowther@nasa.gov  
757-864-4303

Summary of Professional Achievements: My fields of expertise include carbon/boron nitride nanotubes, polymer nanocomposites, electroactive materials, and radiation shielding materials. I am known particularly for my work on dispersion and purification of nanotubes.

Education:  
- BS in Mathematics, Virginia State College

Selected Professional Awards:  
- Whitcomb and Holloway Technology Transfer Award, NASA Langley

Selected Patents and Invention Disclosures:  

Selected Papers and Presentations:  
Mr. Kevin D. Earle  
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NASA Langley Research Center  
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757-864-1913

Summary of Professional Achievements:
I have 9 years of experience performing space systems analysis for the human spaceflight mission directorates and the Science Mission Directorate in the areas of campaign analysis, spacecraft/mission design and analysis, and technology assessment. My work for the human spaceflight mission directorates has primarily focused on development and analysis of human exploration missions and campaigns in an integrated performance, value, cost, and risk context, and has involved me in many of the major human exploration studies since the announcement of the Vision for Space Exploration. I am a member of a systems analysis team actively providing integrated systems analysis support to decision-makers across the agency, including support for the HEOMD-sponsored Human Architecture Team (HAT), HEOMD-sponsored E-M L2 Waypoint Concept, and International Space Exploration Coordination Group (ISECG).

Education:
- B.S. (2005), Aerospace Engineering, Virginia Polytechnic Institute and State University

Selected Professional Awards:
- NASA Systems Engineering Award: Campaign Analysis Team (2011)  
- Superior Accomplishment Award (2): HEFT x2 (2010)  

Selected Study Experience
- Human Exploration Architecture Team, Campaign Analysis and Technology Assessment Support, 2011 to Present  
- International Architecture Working Group, Campaign Analysis Support, 2010 to Present  
- Human Exploration Framework Team, Figure of Merit and Campaign Analysis Support, 2010  
- Constellation Architecture Team, Campaign Analysis Support, 2007-2008  
• Exploration Technology Development Program 2006 Technology Assessment Support, Technology Assessment, 2006
• Exploration Systems Analysis Study, Technology Assessment Support, 2005

Selected Papers and Presentations:
Summary of Professional Achievements:
I have over 10 years’ experience working on the (electrical) transport properties of ceramic and polymeric composite materials. This work has focused on modeling and experimentally verifying relationships between the properties of the constituents, the relative amounts of these constituents, the morphology of the composite and the resulting transport properties. This work has led to over 20 publications in peer reviewed journals and conference proceedings, several patents and numerous data analysis and instrument control software packages in LabVIEW, Python, FORTRAN and Mathematica. I am also a coauthor of an encyclopedia chapter on the electrical properties of nanocomposites.

Education:
• Ph.D. (2005), Physics, University of the Witwatersrand, South Africa
• B.Sc. (Hons) (1999), Physics, University of Zimbabwe

Selected Professional Awards:
• 2010 NASA Langley H.J.E Reid Award for best paper.

Selected Patents and Invention Disclosures:
• J. H. Kang, C. Park, G. Sauti, M. W. Smith, K. Jordan, S. E. Lowther, R. G. Bryant, “High kinetic energy penetrator shielding and high wear resistance materials fabricated with boron nitride nanotubes (BNNTs) and BNNT polymer composites,” Non-Provisional Filing, July 2011.

Selected Papers and Presentations:


Dr. Jin Ho Kang  
Co-Investigator  
National Institute of Aerospace (NIA)  
100 Exploration Way, Hampton VA 23666  
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757-864-9219

Summary of Professional Achievements: I am a senior research scientist for National Institute of Aerospace (NIA) and have been employed at NIA since 2004. My fields of expertise include development of carbon nanotube and boron nitride nanotube related nano-phase materials and biomaterials for aerospace applications. I am known particularly for my work on characterization of mechanical, electric, optical, sensing, energy harvesting, and radiation shielding properties. On these nanomaterials subjects, I hold about 20 patent/invention disclosures. I has authored/coauthored about 20 peer reviewed journal papers and one book chapter. In addition, he has received about 20 awards/recognitions/scholarships from NASA LaRC, NIA, and other government department.

Education:
• Ph.D. in Electrical and Computer Engineering (Chem. Eng.-Material Major), Pohang University of Science and Technology (POSTECH), Korea
• MS in Chemical Engineering, Pohang University of Science and Technology (POSTECH), Korea
• BS in Chemical Engineering, Sogang University, Korea

Selected Professional Awards:
• Richard T. Whitcomb and Paul F. Holloway Technology Transfer Award, NASA Langley
• Best Mentorship Research Site Award (VA New Horizon Governor’s School)
• Korea Science & Engineering Foundation Oversea Scholarship

Selected Patents and Invention Disclosures:
• C. Park, J. H. Kang, K. Gordon, G. Sauti, S. E. Lowther, R. G. Bryant, Doped Chiral Polymer Negative Index Materials (DCPNIM), LAR 18073-1, Jun 2011.
• G. Sauti, C. Park, J. H. Kang, J.-W. Kim, J. S. Harrison, M. W. Smith, K. Jordan, S. E.


Selected Papers and Presentations:

Dr. Cheol Park
Co-Investigator
National Institute of Aerospace
100 Exploration Way, Hampton VA 23666
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757-864-8360

Summary of Professional Achievements: My fields of expertise include carbon/boron nitride nanotubes, polymer nanocomposites, electroactive materials, electrorheology, and bioinspired materials, radiation shielding materials. I am known particularly for my work on dispersion of nanotubes, electrical and dielectric properties of nanocomposites, and sensing/actuation study of nanocomposites. On these nanomaterials subjects, I have more than 40 journal articles (with more than 1600 citations), 2 edited book chapters, over 30 U.S. patents/invention disclosures (7 licensed inventions for 3 different companies), and more than 70 invited lectures at national and international conferences and universities.

Education:
• Ph.D. in Macromolecular Science & Engineering, The University of Michigan
• BS/MS in Textile Engineering, Seoul National University

Selected Professional Awards:
• NASA H. J. E. Reid Award 1st Place (the best paper award of the year), NASA Langley
• Whitcomb and Holloway Technology Transfer Award, NASA Langley
• Best Mentorship Research Site Award (VA New Horizon Governor’s School)
• Korean Government Oversea Scholarship

Selected Patents and Invention Disclosures:
• J. H. Kang, C. Park, G. Sauti, M. W. Smith, K. Jordan, S. E. Lowther, R. G. Bryant, “High kinetic energy penetrator shielding and high wear resistance materials fabricated with boron nitride nanotubes (BNNTs) and BNNT polymer composites,” Non-Provisional Filing, July 2011.

Selected Papers and Presentations: