1. Project Name: **Novel Superhard Materials and Nanostructured Diamond Composites for Multiple Industrial Applications**

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5. **Date Project Initiated and FY of Effort:** FY02, October 1st, 2002; FY02, FY03

6. **Expected Completion Date:** FY08, September 30th, 2008

7. **Project Technical Milestones and Schedule:** (Please provide the milestones/deliverables schedule for your project, both completed and planned.)

FY2004

7-1). Manufacture tungsten carbide bit inserts for rock drilling cones using the reinforced, nanostructured diamond-SiC composite. We plan to use vacuum brazing technique to mount diamond-SiC inserts of different shapes inside tungsten carbide inserts. The wear resistance and impact strength will be measured.

7-2). Synthesize large piece (mm-size) B-C-N superhard bulks and insert them into tungsten carbide bits for reinforcement. The comparative study will be done to test difference of novel B-C-N superhard and diamond-SiC composite in cutting and drilling of various steel, ceramics, geological environments, and other settings.

7-3). Continue to seek strengthening of superhard materials and diamond composites by implanting carbon nanotubes and SiC nanowires. It is expected that outer layers of multiwall carbon nanotubes will react with silicon or h-BN to form SiC or c-BN, leaving a flexible carbon nanotube skeleton inside.

8. **Past Project Milestones and Accomplishments:** (Provide a brief description of progress and accomplishments to date, with specific emphasis on progress towards milestones during the past calendar year.)

A. Bulk nanostructured superhard BC_2N materials

Following the successful synthesis of nanostructured superhard BC_2N bulks at ~ 20 GPa and 2200K in the early last year, we performed the characterization of synthetic superhard BC_2N samples by synchrotron X-ray diffraction, high-resolution transmission electron microscope (TEM), electron energy-loss spectra (EELS), synchrotron infrared (IR) spectroscopy, and Vickers indentation hardness measurements.

B. Nanostructured diamond-SiC composites

In the past half-year, we focused on the preparation of the nanocrystalline diamond and nanocrystalline/amorphous silicon from the microcrystalline materials by ball milling. It was found that the presence of diamond micron size particles in the initial powder mixture promotes milling of silicon particles and their transformation into amorphous state. Nanocrystalline/amorphous silicon, nano-diamond with different grain size (5-100 nm) and their mixture have been successfully obtained. The ultrasonic disperse technology was applied to make the homogeneous mixture of nanocrystalline/amorphous diamond and silicon powder.

C. Boron suboxide

Recently, we carried out the Vickers hardness and fracture toughness of boron suboxide single crystals for the first time. The Vickers hardness of the boron suboxide was found to be very close to that of cubic boron nitride single crystals and its fracture toughness is close to that of diamond. These results show that the boron suboxide and its composites have great potential as new superhard materials for industrial use. Especially, they possess the highest hardness under high temperature (>600 °C) and are thus very important for dry high-speed cutting.

D. Development of the high-pressure equipments

A 500-ton toroidal-anvil press, TAP-98, has been set up. The design for the pressure cell and technical details of the sample assembly for different synthesis process will be finished in this summer. Another new powerful press, 2000-ton multi-application press (TAPLUS-2000), will be delivered to LANSCE-12 at the end of this year.

9. **Planned Future Milestones:** (Outline your R&D plans and schedule for the remainder of the project, with specific emphasis on plans for the next calendar year.)

9-1) Investigate the pressure-temperature region for the formation of the superhard BC_2N phases. It is very interesting and important to explore the influences of the synthesis pressure, temperature and starting material status (composition and crystallinity) on the microstructure, phase fraction and properties of the end products.

9-2) Continue to investigate high *P-T* sintering of large piece (cm-size) diamond-SiC composites in nanocrystalline/amorphous matrix. A starting mixture of diamond, Si, and additional SiC of nanometer size will be used. Sintering of large pieces of diamond-SiC composites with diamond and Si nanopowders as starting materials have the disadvantage in that Si does not react completely with the diamond due to closing of the pores in SiC formed by the reaction of Si with diamond. It is expected that addition of SiC in the starting material (mixture) will bond with the SiC formed by the reaction of Si with diamond and thus reduce the unwanted unreacted Si from the final composite.

9-3) Improve the fracture toughness of nano-structured diamond-SiC composites and novel B-C-N superhard ternary bulks. Reduce the resistivity of diamond-SiC composites by adding metal elements such as Titanium and Nickel to their carbides and make the composites suitable for standard electric discharging machining (EDMable products!).

9-4) Make single crystal diamond with microwave plasma chemical vapor deposition (CVD) method, improve the fracture toughness by tuning the nitrogen percentage and vacancy concentration, adjust the electronic properties of diamond by doping with Boron or Silicon to make p- or n-type semiconductor diamond.

9-5) Perform high *P-T* sintering of superhard B-C-N-O compacts in inch size and tests for their applications as cutting and drilling tools. Compare their mechanical properties and thermal stability with those of diamond, cBN, SiCN, Si_3N_4, BC_2N. Start high P-T synthesis on carbon nitrides.

10. **Issues/Barriers:** (Provide a brief description of any technical problems or barriers encountered and how these problems have been or will be resolved, or significant deviations from original scope and/or budget.)

We are currently getting into a new research field of applying nanotubes and nanowires to reinforce the nanostructured superhard composites. This is a further extension of the proposed work and the purpose of the new study is to improve the fracture toughness of the nanocomposites so that they can be better applied in industrials. The major difficulties are: (1) how to homogeneously disperse the nanotubes with the starting materials; (2) how to form the bonding between nanotubes and the matrix of the composites. Nanotubes have very large modulus to weight ratios and should be very good candidates to reinforce the composites, just like steel reinforcement of concrete. However, the nanotubes are virtually “non-wetting” and are difficult to be anchored, either physically or chemically, onto the matrix. We are exploring the possibility of reactions between amorphous materials and nanotubes to form the string bonds. This study is an extension of the original research scope but with much greater depth. It is apparent that the original budget did not cover this extension and it would be very much appreciated if OIT Program can provide more funding for the current project.

11. **Intended Market and Commercialization Plans/Progress:** (Describe the end-use application and market potential for the research, and the plans and progress for commercial application/adoption, where appropriate; be sure to identify what the product of the research will be and how this product will be introduced/disseminated to the appropriate IOFs.)

Of the diamonds used for industrial purposes today, some 90% of them are synthetic, and 10% natural. The major use of diamond grit is in the machining of stone and concrete. Polycrystalline diamond (pcD) was introduced to the market in the early 1970s, making it available to industry relatively large pieces of diamond, albeit polycrystalline rather than mono-crystalline, at an economical cost. Such materials can be produced with varying mechanical properties and are used in a wide variety of cutting applications. As a cutting tool material, it is predominantly used to machine nonferrous abrasive materials including drilling of rock in oil and gas exploration, and in the engineering and manufacturing industries for the machining of aluminum alloys, reinforced plastics, new wear resistant lightweight composite materials.

In 2000, synthetic diamond production in USA reached 248 million carats (~ 50 tons), a record high for the fourth consecutive year since 1996. The United States remained the world's largest market for industrial diamond in 2000 and the total consumption is about 500 million carats (~ 100 tons) or an equivalent of one billion US$ costs for raw materials. The polycrystalline diamond products used in U.S. cost about half a billion US$ per year, and the finished end use superhard materials products, including cubic boron nitride and diamond, totally valued at approximately five billion US$ in 2000. The United States will continue to be the world's largest market for industrial diamond well into the next decade and to be the major producer and exporter of industrial diamond as well. The most dramatic increase in U.S. demand for industrial diamond is likely to occur in the construction sector as the $200 billion Transpiration Equity Act for 21st Century (Public Law 105-178; enacted June 9, 1998) is further implemented. The act provides funding for building and repairing the Nation's highway system through 2003. Industrial diamond coats the cutting edge of saws used to cut cement in highway construction and repair work.

Due to the poor thermal stability of diamond, it usually needs environmentally hazardous coolants for the cutting/machining applications. The recycling costs of these coolants amount to 10%-40% of the total machining costs. For example, in Germany alone these costs approach one billion US$ per year. Even though in many cases polycrystalline cubic boron nitride does not need the use of coolant, its machining performance is only half of the diamond. Most of the sintered polycrystalline diamond specimens gave hardness values of about 70 GPa, and the Hv values of polycrystalline cubic boron are usually less than 40 GPa. According to our recent experiments, nanocrystalline C-B-N composites have hardness over 60 GPa, comparable to that of diamond but are thermally and chemically more stable than diamond. Therefore, significant economic benefit and energy savings can be achieved by changing to machining/cutting with nanocrystalline superhard C-B-N composites (it is estimated to save over 2 billion US$ per year in U.S.). In addition, environmental improvements can also be achieved since such machining/cutting do not need the use of coolant.

Today, polycrystalline diamond compact (PDC) drills bits account for roughly one-third of the total worldwide rock bit market, with annual sales exceeding $200 million. A PDC bit now holds the all-time record (over 22,000ft) for single-run footage in the same well with no bit maintenance or intervening drilling operations. The benchmark for durability has been set by a PDC bit that achieved the all-time record for cumulative footage by drilling a distance greater than 180,000 ft in 26 runs. Furthermore, the all-time record for penetration rate is attributable to a PDC bit that drilled at more than 2,200 ft/hr.

Drilling cost savings derived from superior PDC bit performance can be dramatic, with savings for a single PDC bit run often exceeding $100,000 in suitable rock formations. Millions of dollars in drilling costs are saved annually in the energy extraction industries through the use of PDC drill bits.

12. **Patents, publications, presentations:** (Please list number and reference, if applicable.)

PATENTS

Bulk Superhard B-C-N Nanocomposite Compact and Method For Preparing Thereof,
Inventors: Yusheng Zhao and Duanwei He, Agent Docket Number: S-97, 739 (pending).

Nano-Structured Diamond/SiC Composites,
Inventors: Jiang Qian and Yusheng Zhao, (in application)

Publications

J. Qian, T. W. Zerda, D. He, L. Daemen, Y. Zhao, Micron diamond composites with nanocrystalline silicon carbide bonding, J. Mater. Res.. 18, 1173-1178 (2003).

Y. Zhao, D.W. He, L. L.Daemen, J. Huang, T. D. Shen, R. B. Schwarz, Y. Zhu, D. L. Bish, J. Zhang, G. Shen, J. Qian, T. W. Zerda. Superhard B-C-N materials synthesized in nanostructured bulks, *J. Mater. Res*., 17, 3139-3145 (2002)

D. He, Yusheng Zhao, L. Daemen, J. Qian, T. D. Shen, T.W. Zerda, Boron suboxide: as hard as cubic boron nitride, *Appl. Phys. Lett.* 81, 643 (2002)

J. Qian, G. Voronin, T.W. Zerda, D. He, Y. Zhao, High pressure high temperature sintering of diamond-SiC composites by ball milled diamond-Si mixtures, *J. Mater. Re.* 17, 2153-2160 (2002)

D. He, M. Akaishi, B. L. Scott, Y. Zhao, Growth of boron suboxide crystals in the $B-B_2O_3$ system at high pressure and high temperature, *J. Mater. Res*. 17, 284-290 (2002).

C. Pantea, J. Qian, G. A. Voronin, and T. W. Zerda, Journal of Applied Physics, Graphitization of diamond crystals at high pressures, Vol. 91, No. 4 (2002) 1957-1962

C. Pantea, J. Gubicza, T. Ungar, G. A. Voronin, and T. W. Zerda, Dislocation density and graphitization of diamond crystals, Physics Review B 66, 094106 (2002)

Highlight

Our study on boron suboxide (*B_6O*) single crystals indicates that boron suboxide is as hard as cubic boron nitride (the second hardest superhard material used in industry) and has fracture toughness similar to that of diamond. Boron suboxide can be synthesized at much lower pressure (even at ambient pressure) compared to the preparation of diamond and cubic boron nitride. This significantly adds to the commercial attractiveness of boron suboxide as a superhard material, and as a competitor of cubic boron nitride and diamond in industrial process. The published work on B_6O (,*Appl. Phys. Lett.* 81, 643, 2002) has attracted a great deal of attention in the materials synthesis community and was highlighted by **Nature Science Update** and **Nature Materials Update** (please see the WebPages: http://www.nature.com/nsu/020722/020722-1.html; and http://www.nature.com/cgi-taf/gateway.taf?g=3&file=/materials/highlights/articles/m020725-2.html, Username/password: portalguest/dilbert). This work was also reported by **Los Alamos Monitor** ("Vying for second hardest" by Roger Snodgrass, reporter of Los Alamos Monitor, on July 26 2002) and numerous other websites (http://www.adit.fr/adit_edition/produits/vigie/br/v77/VMA_77_2.html; http://www3.cosmiverse.com/news/science/0702/science07240205.html; *etc.*)