ADMINISTRATIVE INFORMATION

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

2. **Lead Organization:**
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5. **Date Project Initiated:** October 1st, 2002

6. **Expected Completion Date:** 9/30/2006

PROJECT RATIONALE AND STRATEGY

7. **Project Objective:**

Enhancement of the mechanical performance of materials in terms of hardness, fracture toughness, yield strength, and thermal stability is the objective of the project. In particular, we study B-C-N-O superhard materials and diamond-SiC nano-composites for their great technological advantages of superhardness, wear resistance, thermal stability, and fracture toughness. The success of the project on advanced superhard materials will have significant technological impact for future industrial applications in many fields, such as drilling and cutting.

8. **Technical Barrier(s) Being Addressed:**

The lack of systematic works on mechanical, physical, and crystal structural properties in relation to superhard materials and synthesis conditions has left many questions to be addressed. The P-T phase diagram and best-formation range need to be determined for each particular composition. Ball-milling is a new approach for preparing starting materials of nanoscale amorphous phases. The bulk sample of nanostructured diamond composites and/or B-C-N superhard materials may thus contain superhard amorphous/glassy matrix. However, the shock impacts during the ball-milling process may involve a certain amount of impurities in the starting materials that can alter the properties of synthetic products greatly. We need to work out an effective way to reduce the contamination from the mechanical ball-milling process. It is always beneficial to work at low-pressure range because of the reduced risk of cell assembly failure and the enlarged sample dimensions. The selection of suitable catalysts is very important to low P-T synthesis conditions and to the large-scale production of new superhard materials and diamond composites. However, the selection process is extremely tedious and time-consuming. Effective team effort is essential to conduct multitudinous tests to accomplish such a process. The chemical reaction between diamond and silicon at high P-T conditions is dominated by carbon diffusion from the diamond phase into silicon; otherwise, graphitization of diamonds at low pressure and high temperature may cause serious problems of strength reduction. A better understanding of carbon diffusion and diamond graphitization processes at the nanoscale are essential for making better diamond/SiC composites, which is the potential inserts material for hard rock formation drilling.

9. **Project Pathway:**

An R&D program for the synthesis and characterization of novel superhard/superabrasive materials and nanostructured diamond composites focus on enhancement of the mechanical performance of bulk materials in terms of hardness, toughness, strength, wear resistance, and thermal stability. Novel superhard/superabrasive materials and nanostructured diamond/SiC composites work a lot better in all these aspects. Our work consists of three major parts: (1) Synthesis of novel superhard materials in the B-C-N system and the production of nanostructured diamond/SiC composites at high P-T conditions in large-volume; (2) Characterization of mechanical properties of abrasive hardness, fracture toughness, and yield strength of the synthesized products; (3) Implementation of bulk new superhard materials as machine cutting tools and inserts in rock drill-bits and the exploration of high-tech industrial usage of the products. We use neutron/x-ray diffraction, SEM/TEM, and Raman spectroscopy techniques to study phase diagrams, bonding mechanisms, the initiation and propagation of microcracks, and the structure and morphology of crystalline and amorphous phases in P-T-Composition space. Particular attentions are placed on sample preparation, catalyst selection, reaction kinetics, and property characterization. The ultimate goal of the proposed project is to develop practical methods for producing novel superhard and superabrasive materials and nanostructured diamond composites on a large industrial scale.

10. **Critical Metrics:**

Baseline Metrics and Project Metrics:

- Current fracture toughness of the diamond composites is about 8 MPa $m^{1/2}$.
- Enhanced fracture toughness of the diamond composites to more than 12 MPa $m^{1/2}$.

- Operational temperature for diamond composite is below 1000 K.
- Enhanced operational temperature for diamond composite up to 1300 K.

- Inverse relationship between hardness and fracture toughness for ceramics.
- Increase the fracture toughness while maintaining the superhardness.

PROJECT PLANS AND PROGRESS

11. **Past Accomplishments:**

Our research on nanostructured diamond composites has been very fruitful. The hybrid micron-/nano-diamond composites with nanostructure SiC matrix have greatly enhanced fracture toughness by as much as 50%, from $\boldsymbol{K_{IC}} \approx 8$ MPa·$m^{1/2}$ to 12 MPa·$m^{1/2}$. Our nanostructured diamond composite is already about 20~30% tougher than tungsten carbide, for which the fracture toughness is approximately 9~10 MPa·$m^{1/2}$, a hard and tough material often used for harsh applications where brittle polycrystalline diamond compacts would not work. The measured fracture toughness versus grain size of the SiC matrix data fit the Hall-Petch law quite nicely: $\boldsymbol{K_{IC}} = 8.2 + 17.6 \cdot \boldsymbol{d}^{-1/2}$ (MPa·m$^{1/2}$). To the best of our knowledge, this result is the first experimental evidence showing the nanoscale effect of the composite matrix on the fracture toughness of bulk composite material. An inverse relationship between hardness and fracture toughness is the general rule for most materials. The present experimental study provides a practical way to overcome this limitation and achieves super-hardness and high fracture toughness simultaneously. Such enhancement means that diamond composites can be applied in high dynamic impact situations in deep-well drilling of various rock formations. In addition, we synthesized a ternary B-C-N phase for the first time, which has a hardness only yield to diamond.

We have been vigorously pursuing industrial collaborations in promoting the applications of nanostructured diamond-SiC composites. We have established R&D collaborations with several leading diamond manufacturers, including Smith MegaDianond, U.S. Synthetic, and Ringwood Superabrasive. Based on the preliminary test report from U.S. Synthetic, our nanostructured diamond-SiC composites manifested an equivalent wear resistance compared with their standard products, whereas the true strength of nanostructured diamond-SiC composites relies on the high fracture toughness and thermal stability. We have also collaborated with the Institute of Superhard Materials, Ukraine Academy of Science in searching for an optimum way for the massive production of nanostructured diamond composites. Nanostructured diamond composites have been synthesized at 8-9 GPa and T~ 2000 K in various shapes and sizes. Composites in the shape of triangles, disks, cylinders, pins, oblique triangles, triangles with one convex side, hexagonal rods, and tablets were manufactured. The specimens had low porosity, practically were free of unreacted silicon and there was no measurable graphite content. The products have been brazed to WC inserts. The kinetics of reaction between diamond and the titanium brazing alloy was studied and the optimal brazing temperature was determined. Different brazing atmospheres (inert gas, vacuum) and geometry designs were applied for WC-diamond composite inserts, and a drop weight method was developed for testing the impact strength of these novel inserts. WC-diamond composite inserts were mounted on a cone bit, and the analysis of preliminary rock bit field tests indicated that the gauge inserts failed when top surface of the composite was not exactly on the same level as the top surface of the insert. Reliability of the reinforced inserts can be improved by smoothing the surface of the composites. Brazing composites in an inert atmosphere may result in additional improvements. Design of inserts is in early stage and the composites brazing onto the drill-bit inserts is working.

We have made significant progress on the synthesis and characterization of nanostructured B_6O superhard composite materials in the following aspects:

1. Studied the effect of temperature and pressure on the micro-/nano- structure and phase of the B_6O superhard composite materials;
2. Synthesized nearly pure phase B_6O chunk with nanometer grain size successfully;
3. Determined the equation of state and strength of the B_6O using the synchrotron X-Rays;
4. Measured the hardness of the B_6O phase chunk using nano-indentation techniques.

We are currently summarizing the experimental data on nanostructured B_6O superhard composite materials. The advantage of the B_6O is that it has the hardness close to cubic boron nitride at ambient conditions. It performs a lot better than diamond and cBN at high temperatures. The B_6O nanocomposites will play a great role in high-T dry machining.

Our recent *in-situ* high-pressure synchrotron x-ray diffraction and diamond anvil cell studies on carbon nanotubes have shown very exciting experimental results. Upon cold compression up to 70 GPa, we have successful synthesized a third-form crystalline carbon with superior hardness, high density, and bulk modulus compatible to cubic diamond.

We carried a detailed study of the equation of state, elasticity, and hardness of selected hard superconducting transition-metal nitrides and revealed interesting correlations among their physical properties. Both the bulk modulus and Vickers hardness are found to decrease with increasing zero-pressure volume in NbN, HfN, and ZrN. The computed elastic constants from first principles satisfy $c_{11} > c_{12} > c_{44}$ for NbN, but $c_{11} > c_{44} > c_{12}$ for HfN and ZrN, which are in good agreement with the neutron scattering data. The cubic δ-NbN phase possesses a bulk modulus of 348 GPa, comparable to that of cubic boron nitride, and a Vickers hardness of 20 GPa, which is close to sapphire. These results suggest technological applications of such materials under extreme conditions.

12. **Future Plans:**

We will continue to synthesize/optimize the large quantities of nanostructured diamond-SiC composites needed for the laboratory tests and for use in actual drill bits. The industrial standard test results will compare the samples synthesized under different P-T conditions and with different starting materials. We will arrange the drilling field test for the drill bits made of nanostructured diamond composites. In the synthesis and characterization of novel superhard materials, we will investigate nanostructured B_6O composites with various bonding matrices. A wide range of P-T-t conditions, starting materials, and sample preparation processes will be studied. This particular effort is aimed at high-speed, non-coolant "dry", and fine-precision machining.

* Continue development of the brazing technique. Study kinetics of reaction between diamond and various alloys and determine optimal brazing temperature. Optimization of solver content. Study possibilities of brazing diamond composites to WC inserts in high vacuum with inductance heating.
* Industrial standard impact testing of WC – diamond composite inserts, eliminate redundant impact from the drop weight, and minimize data scattering
* Design several types of WC – diamond composite inserts for application in cone bits. Produce samples of WC – diamond composite inserts and test their impact strength.
* We will continue to synthesize the nanostructured, pure B_6O phase chunk at a pressure up to 15GPa and a temperature up to 1800ºC, measure its hardness, fracture toughness, yield strength, and thermal equation of state.
* Further study of bonding between B_6O phase and c-BN phase and the micro-structure of the interface, aim to obtain excellent mechanical and chemical properties.
* Mapping the residual stress/strain of novel B-C-N ternary phase, nanostructured diamond-SiC composites with neutron and high energy x-ray. The residual stress/strain is strongly correlated with the plastic failure of these materials, especially for crack initiation and propagation. The measurement data can be feedback to structure design, high pressure-high temperature synthesis, and post synthesis treatment to further improve the thermomechanical properties of these superhard materials.

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 strong modulus to weight ratio and should a very good candidate to reinforce the composites, just like steel reinforcement of concrete. However, the nanotubes are virtually "non-wetting" and it is hard to anchor them, either physically or chemically, onto the matrix. We are exploring the possibility of amorphous-nanotube reaction to form the string bonds. This study is an extension of the original research scope, however, with much deep depth.

Date	Milestone/Deliverable	Partner Activities
1/1~9/30 2005	Nanostructured diamond-SiC composites and Residual stress and residual strain mapping	LANL, U.S. Synthetic, and Smith Megadiamond are work closely together on optimizing nanostructured diamond-SiC composites and test them with superhard industry standards. LANL's main focus is starting material design/preparation and RS/S mapping for the composites with neutron and high energy synchrotron x-ray; U.S. Synthetic and Smith Megadiamond are working on HP-HT synthesis and test with industrial standards.
10/1~12/31 2005	Improve brazing technology	LANL & TCU will continue our effort in improving the brazing technology for amounting nanostructured diamond-SiC composites into WC insert. Inductance heating in high vacuum is very promising.
1/1~3/31 2006	Standardize impact strength test	LANL & TCU will improve our drop weight test by eliminating the redundant impact with rebound catch device.
4/1~6/30 2006	WC-nanosturctured diamond-SiC inserts	LANL, TCU, and RBI will work together on designing/improving gauge inserts for roller cone bit
1/1~9/30 2006	B_6O based thermal stable composites	LANL & SUNY-Stony Brook will collaborate on synthesis B_6O based composites with multi anvil press.

13. **Project Changes:**

Narrative Description

After receiving the advice from the review committee in 2004, we adjusted the strategy of our project accordingly by shifting our main focus from exploring new type of novel superhard material to promoting the industrial application of nanostructured diamond-SiC composites. So far, two leading U.S. superhard compacts manufacturers, U.S. Synthetic and Smith Megadiamond, are working on synthesis our starting materials and test the composites with industry standards. We are continuing the collaboration with TCU and RBI on improving the brazing technique and designing/fabricating WC-daimond composites inserts for roller cone bit.

14. **Commercialization Potential, Plans, and Activities:**

Polycrystalline diamond (PCD) was introduced to the market in the early 1970s. This made 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 verity of cutting applications. The polycrystalline diamond products used in U.S. cost about an half billion US$ per year, and the finished end use superhard materials products, including cubic boron nitride and diamond, totally value about five billion US$ in 2000. 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. It has been used predominantly in drilling of rock in oil and gas exploration. 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 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.

The goal of the project is to reinforce inserts for drill bits to increase lifetime and performance. Here we apply two-prong approach. We continuously strive to improve the quality of composites, but in the parallel approach we try to find applications where currently produced composites could be immediately applied. One such application is in single cone bits. The gauge inserts help maintain the same diameter of the borehole. Although the single cone bits represent only about 1-2% of the total number of drill bits sold in the US, their role is extremely important. They are typically used in deep holes when the diameter of the well is reduced and where the rock formations are very hard. The single cone bits rotate at a rate smaller than the pipe rotation, about 66 rotations of the drill head per 100 revolutions of the pipe. The weight applied is usually greater than that for the three cone bits. These are conditions best suited for inserts reinforced with diamond composites. Gauge inserts are located on the sides of the drill bit and therefore are not exposed to large impacts. They are however continuously working against very hard sides of the wells where their superior wear resistance is highly desired. We plan to produce another experimental single cone drill bit and test it during deep-hole drilling. If the results are satisfactory production of single cone bits will immediately follow. We also plan to work on improving inserts that could be used as cutting teeth for three-cone bits. Here the challenge is more difficult because the cutting inserts are exposed to large impacts and require high fracture toughness and better mounting techniques.

15. **Patents, Publications, Presentations:** (Please list number and reference, if applicable. If more than 10, please list only 10 most recent.)

Filed 2 Patents -

BULK SUPERHARD B-C-N NANOCOMPOSITE COMPACT AND METHOD FOR PREPARING THEREOF,
Inventors: Yusheng Zhao & Duanwei He, U.S. Patent No. 6,759,128 Issued July 6, 2004

DIAMOND-SILICON CARBIDE COMPOSITE AND METHOD FOR PREPARATION THEREOF,
Inventors: Jiang Qian and Yusheng Zhao, Agent Docket Number: S-100,575 (*pending*)

More than 10 Publications -

Pantea, C., G.A. Voronin, T.W. Zerda, J. Zhang, Y. Zhao, Kinetics of SiC formation during the reaction between diamond and silicon, *Diamond and Related Materials.,* (2005)

Chen, X.J., V.V. Struzhkin, Z.G. Wu, M. Somayazulu, J. Qian, S. Kung, A.N. Christensen, Y. Zhao, R. Cohen, H.-k. Mao, and R. J. Hemley, Hard superconducting nitrides, *Proc. Natl. Acad. Sci*., 2005

Wang, Z., Y. Zhao, P. Lazor, H. Annersten and S. K. Saxena, In-situ Pressure Raman spectroscopy and mechanical stability of superhard boron suboxide, *Applied Physics Letters,* **86**, 041911, 2005.

Wang, Z. Y. Zhao, K., Tait, X. Liao, D. Schiferl, C.S. Zha, R.T. Downs, J. Qian, Y. Zhu, T.D Shen, A quenchable superhard corbon phase synthesized by cold compression of carbon nanotubes, *Prec. Natl. Acad. Sci.*, Vol.101, No.38, 13699-13702, (2004)

Brazhkin, V., N. Dubrovinskaia, M. Nicol, N. Novikov, R. Riedel, V. Solozhenko, and Y. Zhao, What does “Harder than Diamond” mean?, *Nature Materials*, vol.3, pp. 576-577, (2004)

Yan, C-s., H-k. Mao, W. Li, J. Qian, Y. Zhao, & R.J. Hemley, “Ultrahard diamond single crystals from chemical vapor deposition” *Phys. Stat. Sol*. (a) 201, R25– R27 (2004) .

Wang, Z., Y. Zhao, D. Schiferl, C. Zha, R. Downs, Pressure induced increase of particle size and resulting weakening of elastic stiffness of CeO2 nanocrystals, *Applied Physics Letter* (2004), 85, 124-126.

Wang, Z., K. Tait, Y. Zhao, D. Schiferl, C. Zha, H. Uchida, R. Downs, Size-induced reduction of transition pressure and enhancement of bulk modulus of AlN nanocrystals, *Journal of Physical Chemistry B* (2004), Vol.108, No.34, pp. 11506-11508.

Qian J., C. Pantea, J. Huang, T. W. Zerda, and Y. Zhao, Graphitization of diamond of different sizes at high pressure-high temperature. *Carbon*, Vol 42/12-13 pp 2691-2697 (2004).

Y. Zhao, J. Qian, L. L. Daemen, C. Pantea, J. Zhang, G. A. Voronin, and T. Waldek Zerda, Enhancement of fracture toughness in nanostructured diamondSiC composites, Applied Physics Letters, Vol. 84, No. 8 (2004).

Many Presentations and Invited Talks -

Milestone Status Table:

ID #	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Novel Superhard B-C-N Materials			
1.1	Synthesis BCN, BC_2N and BC_4N	6/30/02	6/30/02	Done
1.2	Characterization of BC_2N & BC_4N	9/30/02	9/30/02	Done
1.3	Publish Data on B-C-N System	12/30/02	12/30/02	Done
2	Novel Superhard B_6O Materials			
2.1	Synthesis B_6O crystals	3/30/02	3/30/02	Done
2.2	Characterization of B_6O crystals	6/30/02	6/30/02	Done
2.3	Publish Data on B_6O crystals	9/30/02	9/30/02	Done
3	Diamond-SiC Nanocomposites			
3.1	Synthesis Nano- Diamond-SiC	12/30/02	12/30/02	Done
3.2	Characterization of Diamond-SiC	6/30/03	6/30/03	Done
3.3	Publish Data on Diamond-SiC	12/30/03	12/30/03	Done
3.4	Optimize Diamond-SiC Synthesis	3/30/04	3/30/04	Done and on-going
3.5	More Publication on Diamond-SiC	9/30/04	9/30/04	Done

ID #	Task / Milestone Description	Planned Completion	Actual Completion	Comments
4	B_6O Nanocomposites			
4.1	Synthesis B_6O Nanocomposites	3/30/04	3/30/04	Done
4.2	Characterize B_6O Nanocomposite	6/30/04	6/30/04	Done
4.3	Optimize B_6O Synthesis Condition	9/30/04	9/30/04	Done and on-going
4.4	Publish Data on Nano- B_6O	12/30/04	12/30/04	Done

ID #	Task / Milestone Description	Planned Completion	Actual Completion	Comments
5	Drill-Bits of Nano- Diamond-SiC			
5.1	Bulk Production of Diamond-SiC	3/30/04	3/30/04	Synthesized
5.2	Industrial Test of Diamond-SiC	13/31/04	12/31/05	Delayed due to our industrial partner's tight production schedule
5.3	Mount Diamonds on WC inserts/Drill-Bits	9/30/04	9/30/04	Done
5.3	Arrange Field-Tests of Drill-Bits	12/30/04		Coordination critical
5.4	Marketing of Diamond Drill-Bits	9/30/06		Need expert helps
6	Machining Tools of Nano- B_6O			
6.1	Bulk Production of Nano- B_6O	3/30/05		Depend on Lab results
6.2	Brazing Nano- B_6O on Tools	9/30/05		
6.3	Industrial Test of Nano- B_6O	3/30/06		
6.4	Marketing of Diamond Drill-Bits	9/30/06		Need expert helps