

ADMINISTRATIVE INFORMATION

1. **Project Name:** Novel Superhard Materials and Nanostructured Diamond Composites for Multiple Industrial Applications (CPS# 1795)
2. **Lead Organization:** Los Alamos National Laboratory
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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:**

This project focuses on the enhancement of the mechanical performance of materials in terms of hardness, fracture toughness, yield strength, and thermal stability is the objective of the project. The research focuses on the large-scale industrial applications of drilling and cutting. In particular, we study B-C-N-O superhard materials and diamond-SiC nano-composites for their great technological advantages of 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.

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.

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, and wear resistance. 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 pressures and high temperatures 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 Technical Metrics:**Baseline Metrics:**

- Current fracture toughness of the diamond composites is about 8 MPa m^{1/2}.
- Operational temperature for diamond composite is below 1000 K.
- Only diamond and cubic boron nitride have the hardness over 40 GPa.
- Inverse relationship between hardness and fracture toughness for ceramics.
- Drill bit changing when encountering different (soft & hard) rock formations.

Project Metrics:

- Enhanced fracture toughness of the diamond composites to more than 12 MPa m^{1/2}.
- Enhanced operational temperature for diamond composite up to 1300 K.
- Novel superhard B₆O materials in nanostructured composite forms.
- Increase the fracture toughness while maintaining the superhardness.
- One superhard and ultratough drill bit to work on all rock formations and last longer.

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 $K_{IC} \approx 8 \text{ MPa}\cdot\text{m}^{1/2}$ to $12 \text{ MPa}\cdot\text{m}^{1/2}$. 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: $K_{IC} = 8.2 + 17.6\cdot d^{-1/2}$ (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.

We have been vigorously pursuing industrial collaborations in promoting the applications of nanostructured diamond-SiC composites. The hybrid micron-/nano-diamond composites with nanostructure SiC matrix provide a practical way to achieve 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. We have established R&D collaborations with several leading diamond manufacturers, including Smith MegaDiamond, U.S. Synthetic, and Ringwood Superabrasive. 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 mounted on the drill bits of Rockbit International – Gearhart, our industrial partner, for well-drill field tests. A series of diamond composites are vacuum brazed to WC inserts. Analysis of 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.

12. Future Plans:

We will continue to synthesize 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 titanium and determine optimal brazing temperature. Optimization of solver content. Study possibilities of brazing diamond composites to WC inserts in different inert atmospheres.
- * Industrial standard impact testing of WC – diamond composite inserts and testing inserts
- * 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 nanostructure, pure B₆O phase chunk at a pressures up to 15GPa and a temperature up to 1800°C.
- * The nano-indentation measurements will get the hardness of the B₆O chunk, and the micro-hardness and fracture toughness data will be measured.
- * The measurements of the thermal equation of state and the yield strength of B₆O at high pressure and high temperature conditions will be conducted;
- * Further study of bonding between B₆O phase and c-BN phase could and micro-structure interface, hopefully to obtain excellent mechanical and chemical properties.

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.

13. Project Changes:

The superhard materials project has been extended into nanotube reinforcement study for ultratoughness.

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 variety 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:

Filed 2 Patents -

BULK SUPERHARD B-C-N NANOCOMPOSITE COMPACT AND METHOD FOR PREPARING THEREOF,

Inventors: Yusheng Zhao & Duanwei He, Agent Docket Number: S-97, 739 (*allowed*).

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 -

1. 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)
2. G. A. Voronin, T. W. Zerda, J. Qian, Y. Zhao, D. He, and S. N. Dub. Diamond-SiC nanocomposites sintered from a mixture of diamond and silicon nanopowders. *Diamond and Related Materials*, Vol. 12/9, pp. 1477-1481, 2003.
3. G. A. Voronin, C. Pantea, T. W. Zerda, J. Zhang, L. Wang, and Y. Zhao. In situ X-ray diffraction study of germanium at pressures up to 11 GPa and temperatures up to 950 K. *Journal of Physics and Chemistry of Solids*, Vol. 64, pp. 2113-2119, 2003
4. G. A. Voronin, C. Pantea, T. W. Zerda, L. Wang, and Y. Zhao. In situ X-ray diffraction study of silicon at pressures up to 15.5 GPa and temperatures up to 1073 K. *Physical Review B*, Vol.68, pp. 020102-1 – 020102-4, 2003.
5. Micron diamond composites with nanocrystalline silicon carbide bonding J. Qian, T. W. Zerda, D. He, L. Daemen, Y. Zhao, *Journal of Material Research*, Vol. 18, No. 5 (2003) 1173-1178
6. C. Pantea, J. Gubicza, T. Ungar, G. A. Voronin, and T. W. Zerda. High pressure effect on dislocation density in nano-size diamond crystals. *Diamond and Related Materials*, (in press).
7. G. A. Voronin, C. Pantea, T. W. Zerda, L. Wang, and Y. Zhao. Thermal equation of state of osmium: a synchrotron X-ray diffraction study. *Journal of Physics and Chemistry of Solids* (submitted).

8. G.A. Voronin, T.W. Zerda, J. Gubicza, T. Ungár, and S. N. Dub. Properties of nanostructured diamond – silicon carbide composites sintered by high-pressure infiltration technique. *Journal of Material Research* (submitted).
9. Graphitization of diamond of different sizes at high pressure-high temperature, J. Qian, C. Pantea, T. W. Zerda, Y. Zhao, submitted to *Carbon*
10. 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).

Many Presentations and Invited Talks -