U.S. Department of Energy
Energy Efficiency and Renewable Energy

# Novel Superhard Materials and Nanostructured Diamond Composites for Multiple Industrial Applications (*CPS# 1795*)


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Smith MegaDiamonds
Ringwood Superabrasives
Rock Bit International


**DOE_ITP-IMF 2005 Materials Project and Portfolio Review Meeting**
**June 1-3, 2005, Wyndham Hotel, Chicago, IL**

# Novel Superhard Materials and Nanostructured Diamond Composites for Multiple Industrial Applications (*CPS# 1795*)

**Goal:** Develop superhard inserts materials for drill bits / cutting tools.

**Challenge:** Current cobalt-based polycrystalline diamond compacts lack the thermo-mechanical stability for hard rock/abrasive formations.

**Benefits:** Improve drill efficiency, reduce drill time, and lower drill cost by a factor of 2~3; energy savings of 27~70 trillion Btu/year after commercialization.

**Potential Applications:** Thermal stable polycrystalline diamond compacts (PCD) or boron-based compounds ($B_6O$, $BC_2N$) inserts for drill/machinery industry.

**FY06 Activities:** Evaluate polycrystalline diamond or boron-based compound inserts with industrial standards; tipped inserts into drill bit for field test; further optimize the thermo-mechanical properties of the superhard inserts; design and build drill bit with these novel inserts.

# Novel Superhard Materials and Nanostructured Diamond Composites

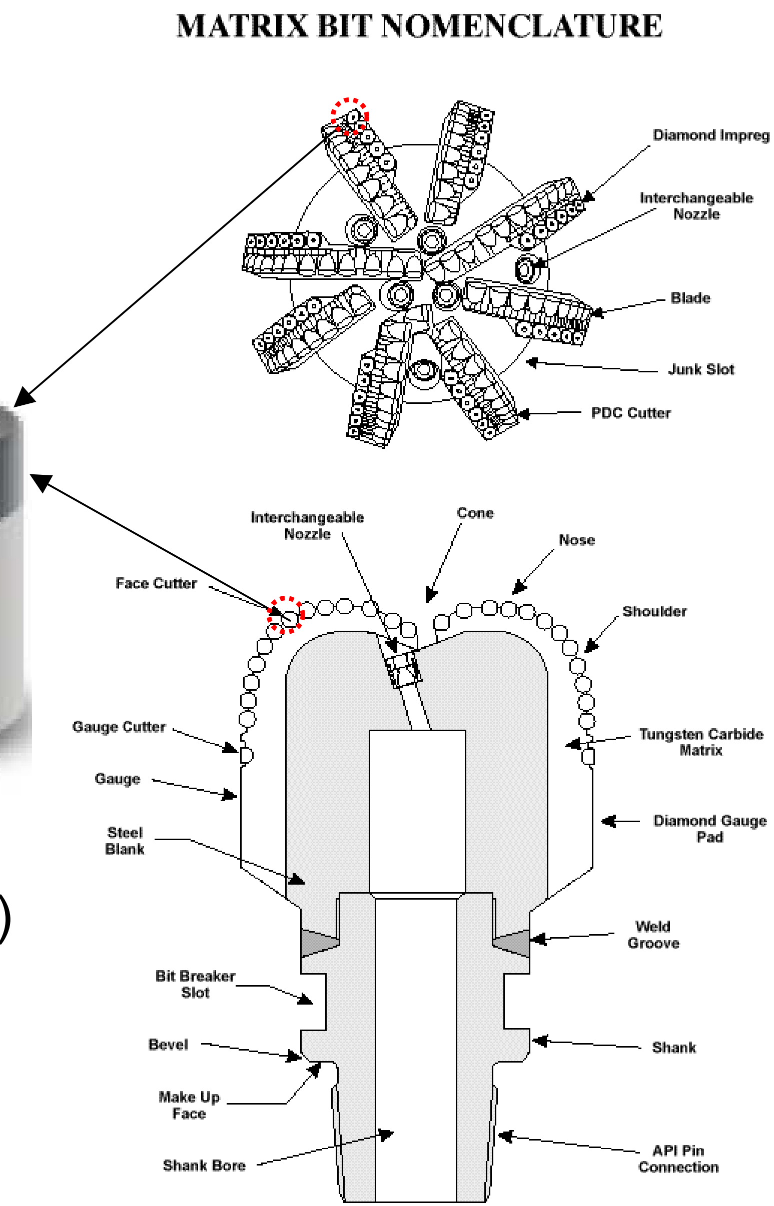
## Background of PDC technology

### Functional material criteria:

- Hardness (wear resistance)
- Strength (polycrystalline)
- Fracture toughness
  *resistance to cracking*
- Thermal stability (?)

⇣

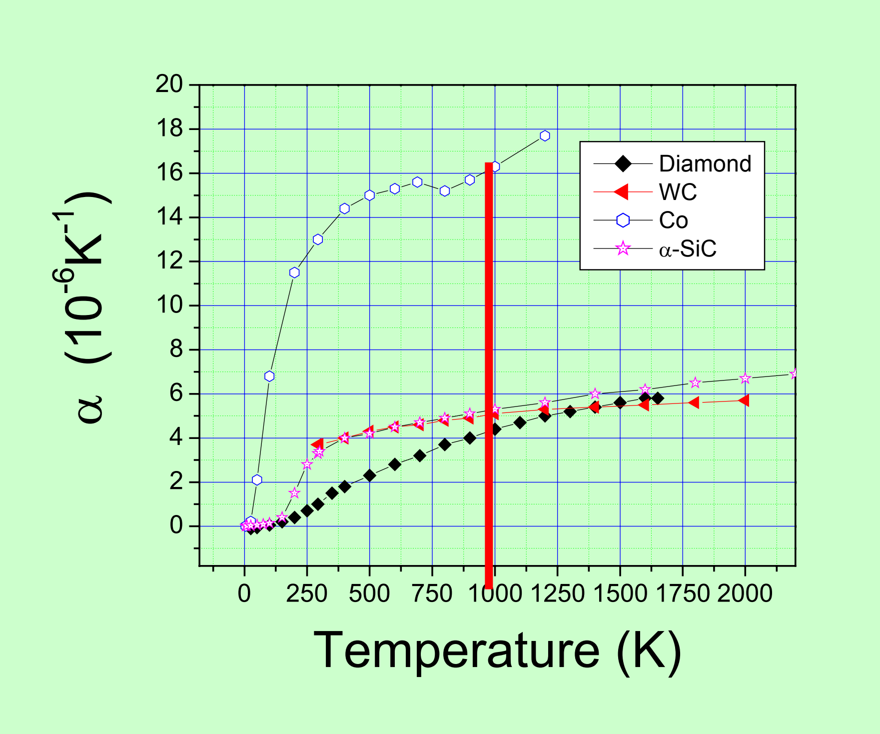
- Bulk piece

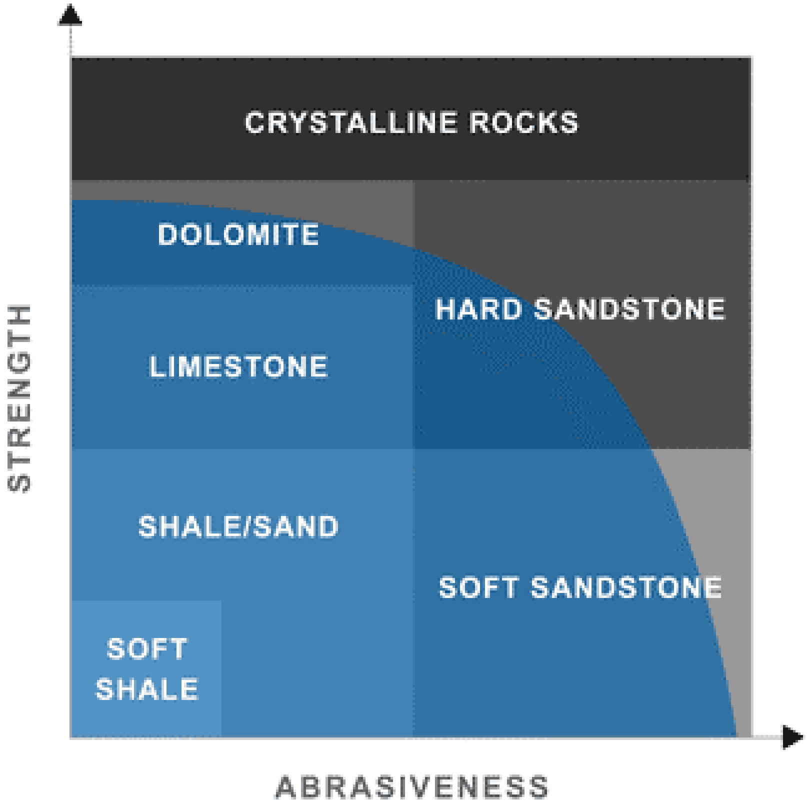



### PDC drilling:

~40% of total footage in USA ($10 billion/year)
~50% of total footage worldwide

# Challenge of PDC technology: *hard rock/abrasive formations*!




**Thermomechanical failure:**

- Cobalt promotes diamond graphitization
- Difference of thermal expansions among cobalt,WC, and diamond

Smooth wear → micro-chipping →

gross fracturing→ delamination

# *Industrial Needs (Pain):*

Blunting and shattering of the cutting edges and drilling bits greatly slow down the machining and penetrating processes.

***— waste time & energy***

*Conventional diamond compacts*

- Metal bonding (Cobalt, Nickel, …)
- Low thermal stability ($T_G$< 900ºC)
- Low fracture toughness (< 8 MPa·$m^{1/2}$)

*Nanostructured diamond composites*

- Ceramic bonding (SiC, TiC, …)
- High thermal stability ($T_G$>1200ºC)
- High fracture toughness (>12 MPa·$m^{1/2}$)

# *Technological Solution (Pill):*

Harder, tougher, last "forever" superhard & superabrasive materials to speed up the machining and drilling processes.

***— increase efficiency***

# Barrier-Pathway Approach

### *Barriers*

- Low thermal stability (1000K) of cobalt based PDC inserts due to catalyst effect and difference in thermal expansion
- Lack of strong, tough, and thermal stable inserts for hard rock/abrasive drill formations

### *Pathways*

- Development of diamond/SiC and boron compound based tough thermal stable inserts
- Test thermal-stable and tough insert with industrial standards
- Braze thermal stable and tough inserts into drill bit for field test
- Optimize inserts and implement tough and thermal stable drill technology

### *Critical Metrics*

- Thermal stable up to 1500K
- Lower the drill cost by a factor of 2~4

| **Benefits (*est. for drill industry only*)** | **Annual** |
|---|---|
| **Energy Savings** | **27~70 trillion Btu** |
| **Cost Savings** | **$200~500 million** |

# Novel Superhard Materials and Nanostructured Diamond Composites

## Novel thermally stable inserts

### Diamond/SiC inserts: SiC ↔ cobalt!

- **Wear/abrasion resistance:**
  Hardness ($E$ and $H_v$)
  Self-sharpening mechanism
  ~$1 \times 10^6$ *versus* Barre Granite
- **Impact strength (toughness):**
  nanocrystalline SiC matrix
  12 MPa/m$^{1/2}$ > (WC ~ 10 MPa/m$^{1/2}$)
- **Thermal stability (1500K):**
  Graphitization eliminated (Co → SiC)
  Difference in thermal expansions ↓

### Boron based compounds

B-C-N ternary phase ($BC_2N$, $BC_4N$)

- Second hardest ($H_v$=60 GPa)

Boron suboxide ($B_6O$)

- As hard as cBN ($H_v$=45 GPa)

Chemical inertness
Thermal stability (1800K)
Hugh potential for drilling, machining, cutting…

# Nanostructued diamond-SiC composites

**Starting material :**

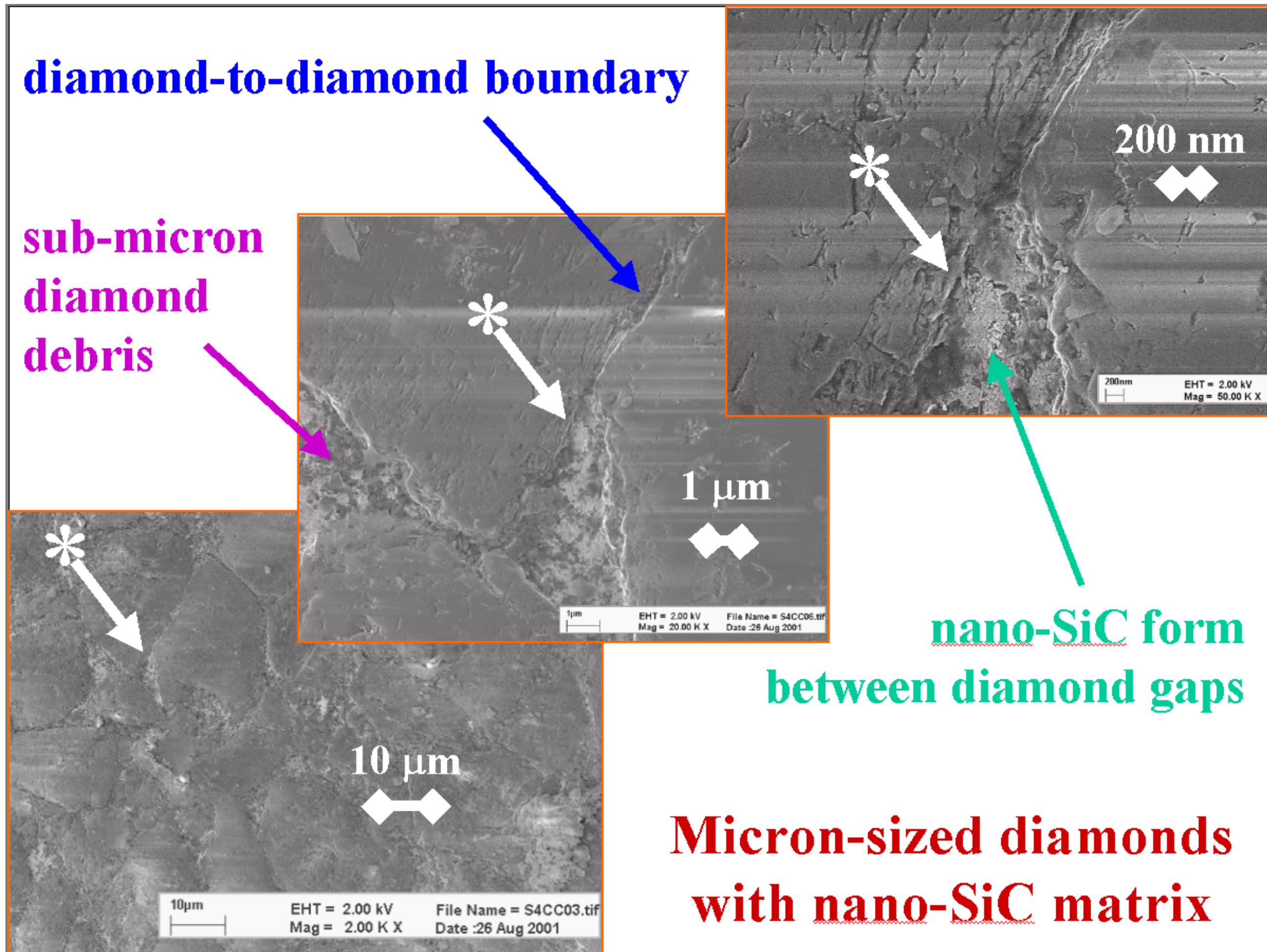
- micron/nano diamond + silicon mixture
- high energy ball milling
- optimized packing
- EDMable with Ti/B doping

**HP-HT reactive sintering:**

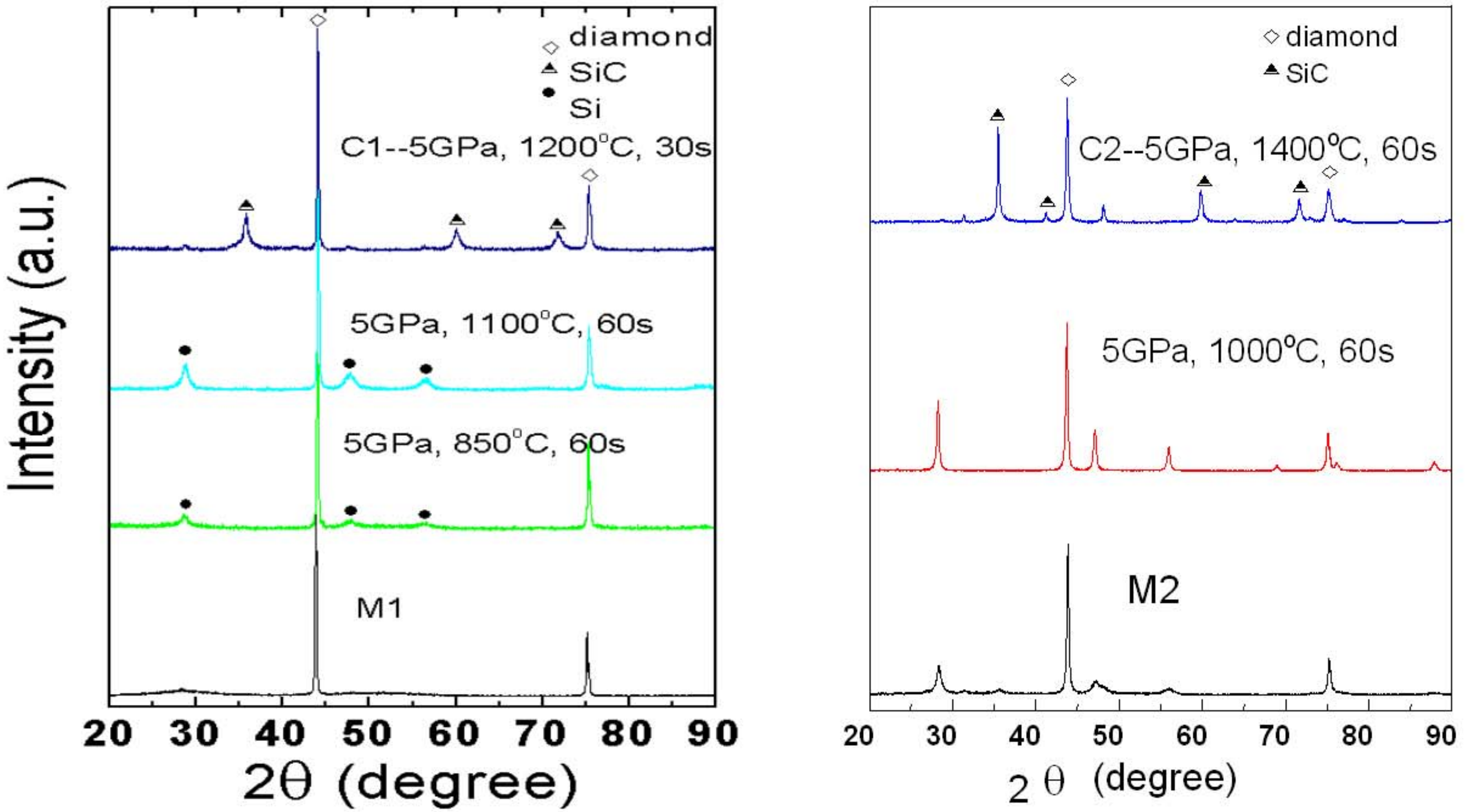
- 5~7 GPa, 1800~2000 K

**Final product:**

Micron diamond +nano SiC matrix



# Thermally Stable Diamond-SiC Composites with Nanocrystalline Bonding Matrix



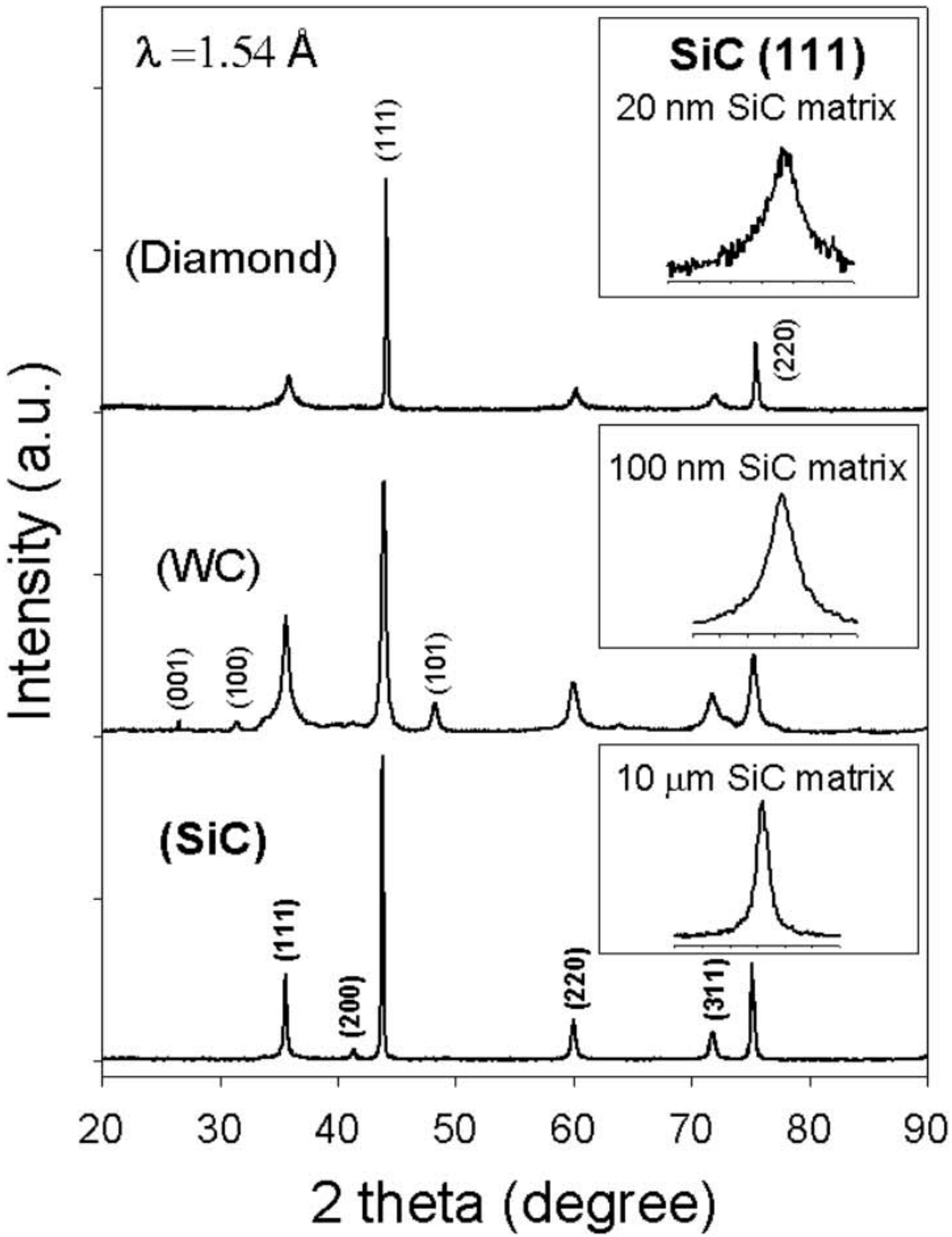

**High *P-T* reactive sintering !!!**

**carbon (*diamond*) and amorphous silicon**

**to form nanocrystalline silicon carbide (SiC) matrix**

# Diamond-SiC composites

synthesis condition: 5 GPa, 1800 K, 30 sec




We tested three sample preparation procedures for high *P-T* synthesis of diamond-SiC composites:

1) a thorough mixture of diamond and amorphous silicon;
2) thorough wet mixing of nano-diamond & silicon in methanol;
3) Si-melt infiltration into diamond aggregates under high *P-T*.

The resulting products have distinct SiC matrices of various grain sizes: 20nm, 100nm, and 10,000nm, respectively.

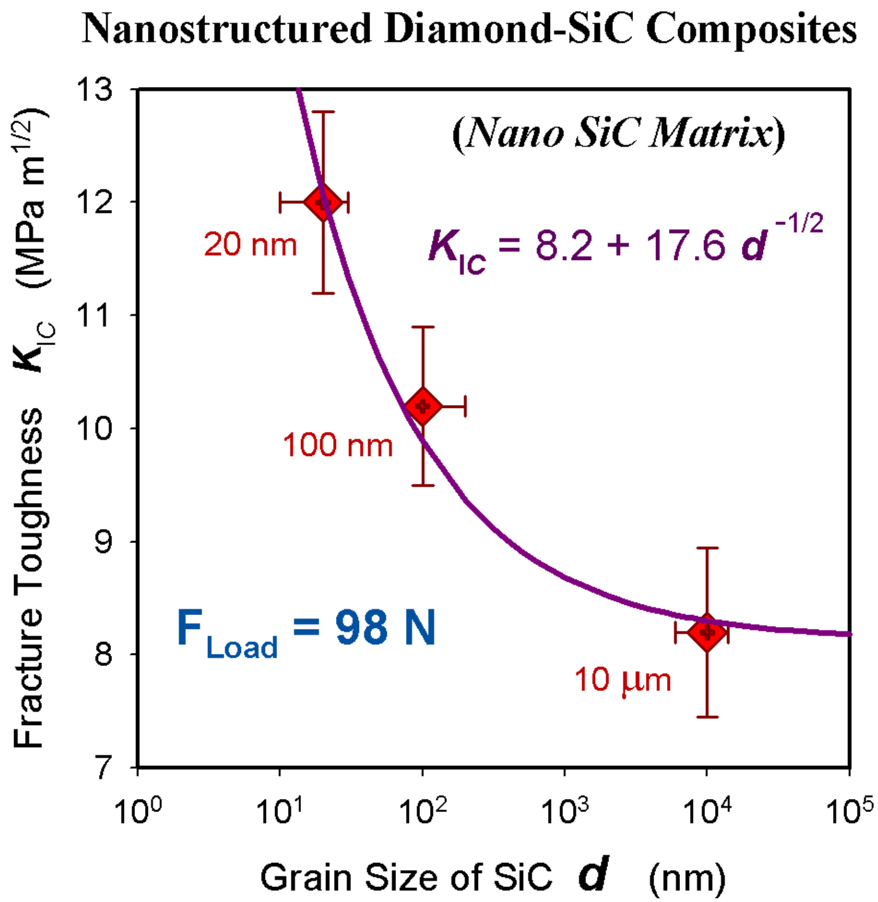
The diamond participation speeds up the Si amorphisation process significantly

Overcome the "bottle-neck" problem of the infiltration method.

# Novel Superhard Materials and Nanostructured Diamond Composites

## Much improved fracture toughness!

**Improvement of G-Ratio ?!**
**(*high quality diamonds*)**
**(*cubic anvil sintering*)**




**Subject: nano-diamond composite material**
**Date: Fri, 27 May 2005 15:44:38 -0600**
**From: "Ken Bertagnolli" <kbertag@ussynthetic.com>**
**To: "Yusheng Zhao " <yzhao@lanl.gov>**
**"Jiang Qian" <jiangq@lanl.gov>**

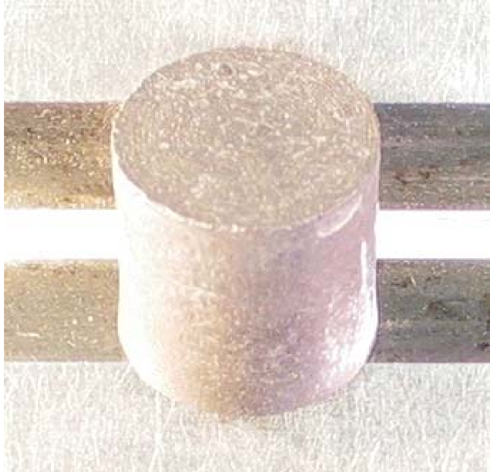
**Yusheng and Jiang,**

**We have pressed one sample of your nano-diamond composite material. The purpose of this run was to check the HTHP cell design. The attached photo shows the diamond cylinder after the test. This part was taken to 1400C for about 1 minute, and the cell behaved normally. The resultant material appears to be very hard and well consolidated. We are now ready to load and run the remaining samples. We will make three runs of each powder type. I d like to run one at 1400C, one at 1500C, and one at 1600C. We can then test the performance of each condition. How does this sound to you?**

**Regards,**

**Ken Bertagnolli**

**kbertagnolli@ussynthetic.com**



# PCD Enhanced Insert Impact on WC-Co Anvils

*Dan Belnap, Ph.D.*
R&D Manager, Smith Megadiamond

***Diamond and Related Materials**, (unpublished)*

***The carbide was observed to transition from localized plastic deformation at lower impact loads to severe cracking and deformation at high impact loads.***

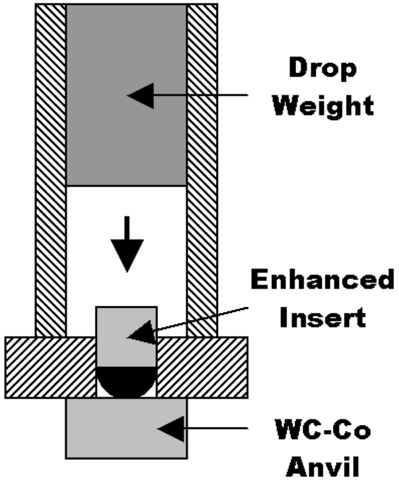



Figure 1. Impact testing schematic.

**LANL and Smith MegaDiamond and U.S. Synthetic have signed agreements to transfer starting materials for industrial synthesis and to further conduct mechanical test using industrial standards.**

**Impacting, Drilling, Cutting Tests on Granites & Limestone**

***In contrast to the WC-Co anvils, the enhanced polycrystalline diamond insert damage was relatively minor, observed during impact testing.***

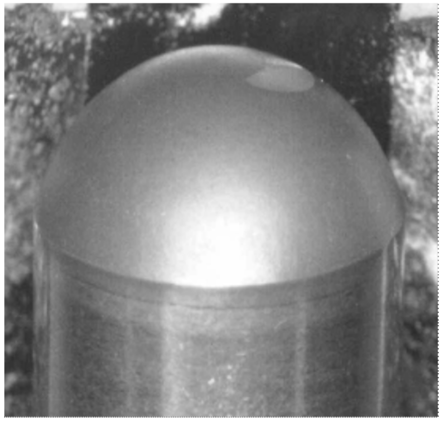
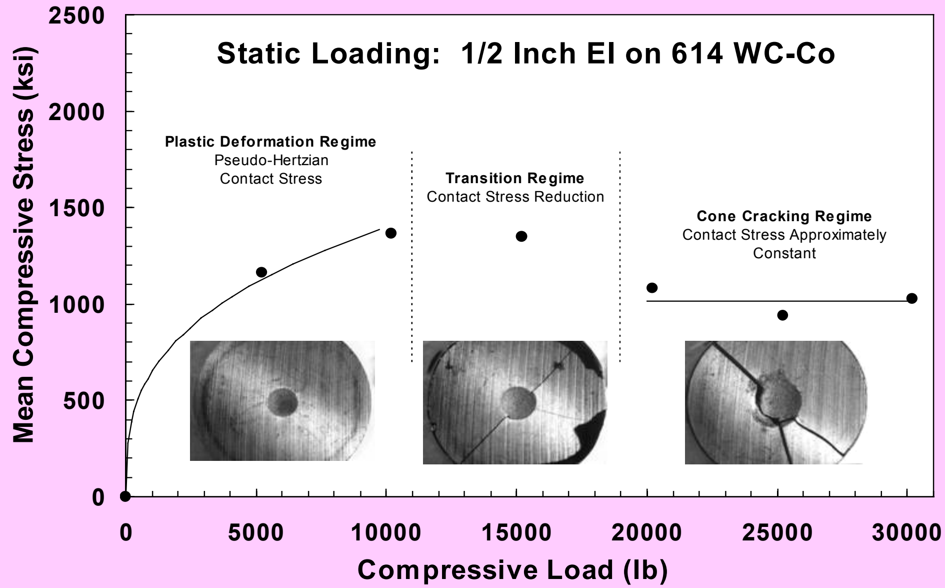


Figure 3. Enhanced insert with impact damage.



# *Case Study – Oil Drilling*

to drill a 7000 feet depth well in East Texas (*average well 5500 feet* )

- **Conventional bit**

Soft rock formation:
PCD bit, 100 ft/h

Hard rock formation:
WC bit, 20 ft/h

Down-time to change bit
24 ~ 48 hour

Danger of abandon the well

- **Novel nano-composites diamond bit**

Soft & hard rock formation
One bit, 150 & 100 ft/h
Less bit changing

- 7 bits reduced to 4 bits
- 6 trips reduced to 3 trips
- time/energy/money saving 2 ~ 4 times

- Total well drilling in U.S. is 150~180 million feet per year
- It costs $40~50 Billion annually for average $300 per feet
- Total cost for petroleum industry is about $10 Billion/year

Cost saving (*annual*) with adopting novel nano-composite bits can be as much as $300 ~ $500 million per year (*U.S. drilling industry alone*!)

Tuesday, December 16, 2003

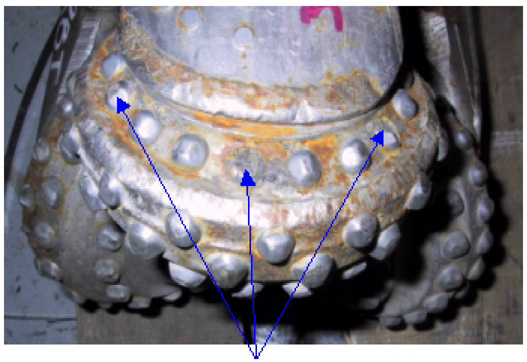
# Canadian Drill Site
# Oil Well Drilling

A quick examination of the returned Canadia ungsten carbide inserts revealed the following

| Number of Composite Inserts | Number of Tungsten Carbide Inserts | Number of failed Composite Inserts | Number of failed Tungsten Carbide Inserts |
|---|---|---|---|
| 18 | 36 | 5.5 | 1 |

One can see that the percentage of failed composite inserts is much higher (5.5/18 = 31%) as opposed to the number of failed Tungsten Carbide inserts (1/36=3%). The rows on the rockbit where both of these inserts were placed is a row which is not considered to be a main cutting row. They were placed in the reaming gage row, which should experience much lower load forces as opposed to the main cutting rows of a rockbit.

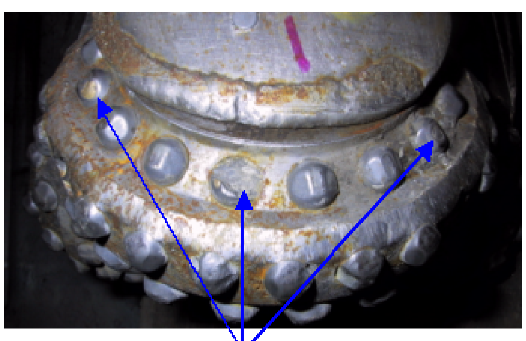
The two photos below show two of the rollercones that had the composite inserts in them



Composite inserts, the two on the right have fractured and failed. The Tungsten Carbide inserts between them are unaffected.

# RockBit International

Composite inserts on the ends are intact while the insert in the middle has fractured.



**USSynthetic** Technical Report

| TITLE: Evaluation of LANL Nano-Structured Diamond Composite Material | | |
|---|---|---|
| AUTHOR: Ken Bertagnolli | DATE: January 22, 2004 | REPORT NO.: KEB-01-2004 |


**SUMMARY**

The purpose of this investigation was to evaluate the performance of five nano-structured diamond composite samples supplied by Los Alamos National Laboratory and determine their suitability for the oil and gas drilling market. The following conclusions can be made from this investigation:

- The wear resistance of the LANL samples was 100 times less than a standard US Synthetic PDC product, much too low for drilling applications.
- The LANL samples had insufficient strength for drilling applications. One sample cracked in half, one sample had a major crack through the center, and another sample generated cracks in the wearflat during the granite-log abrasion test.
- Two of the five samples lacked sufficient edge quality to conduct meaningful tests.

Overall, the LANL samples lack sufficient strength and wear resistance to be applicable to the oil and gas drilling market. Future development to improve these properties could make this material more suitable to the harsh downhole drilling conditions.


***Improvements are desperately needed!***

**INTRODUCTION**

Five nano-structured diamond composite samples were given to US Synthetic by Dr. Yusheng Zhao of Los Alamos National Laboratory on November 17, 2003. The composition of each sample is summarized in Table 1.

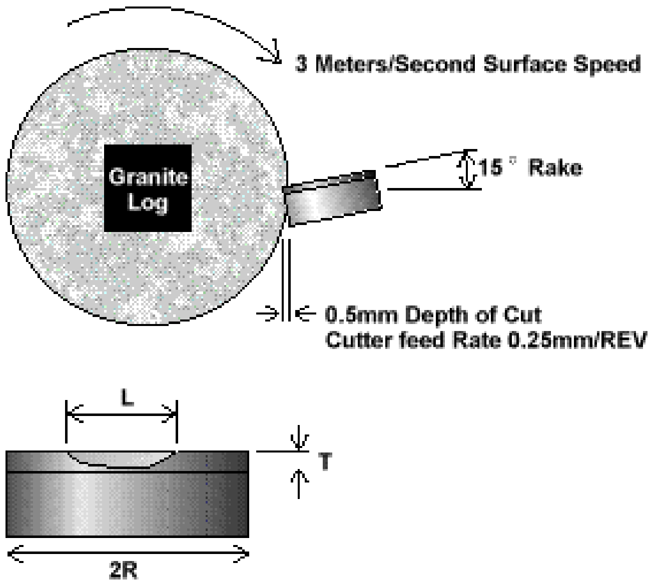
**Table 1. LANL sample composition.**

| | Description | Observations |
|---|---|---|
| 1 | 5-10 micron diamond (70 wt%) + 100nm diamond (10 wt%) + silicon (20 wt%) | Ground edge with some wearflats, possibly a previous wear test |
| 2 | 5-10 micron diamond (70 wt%) + 100nm diamond (10 wt%) + silicon (20 wt%) | Unground, rough edge, not suitable for testing. |
| 3 | 5-10 micron diamond (70 wt%) + 100nm diamond (10 wt%) + silicon (20 wt%) | Ground edge with five hardness indenter marks and cracks. |
| 4 | 250 nm diamond (75 wt%) + 5nm diamond (5 wt%) + silicon (20 wt%) | Ground edge. |
| 5 | 250 nm diamond (75 wt%) + 5nm diamond (5 wt%) + silicon (20 wt%) | Ground edge with many edge chips and a large crater on one side, not suitable for testing. |

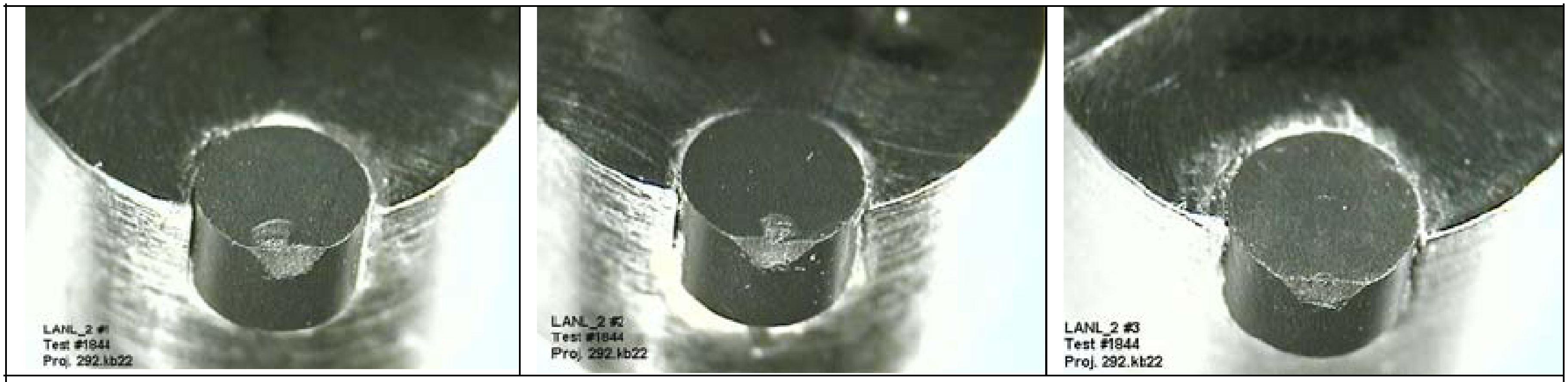
# Novel Superhard Materials and Nanostructured Diamond Composites

## Wear resistance test (*industrial standard*)

| | Granite-Log Test |
|---|---|
| Rotary Speed | 150 RPM |
| Cutting Speed | 400 ft/min |
| Depth of Cut | .010 in |
| In-Feed Rate | .052 in/rev |
| Linear Distance Cut | 2,600 ft |
| Cutter Back Rake | 15 degrees |
| Volume of Rock Cut | 16 $in^3$ |
| Rock Type | Barre Granite |

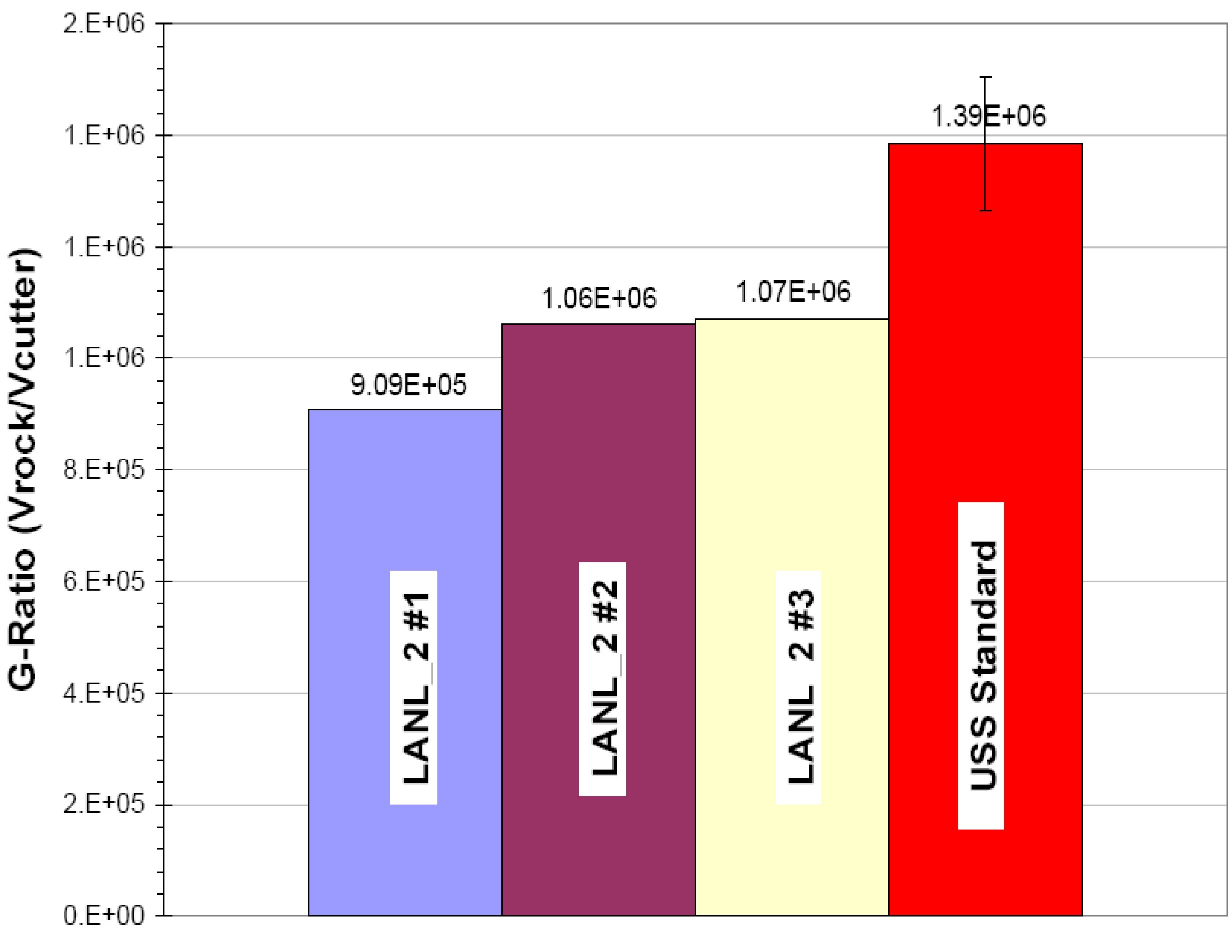



Volume Of Diamond Removed = $T/12R \times (L^2/2 + T^2)^{3/2}$



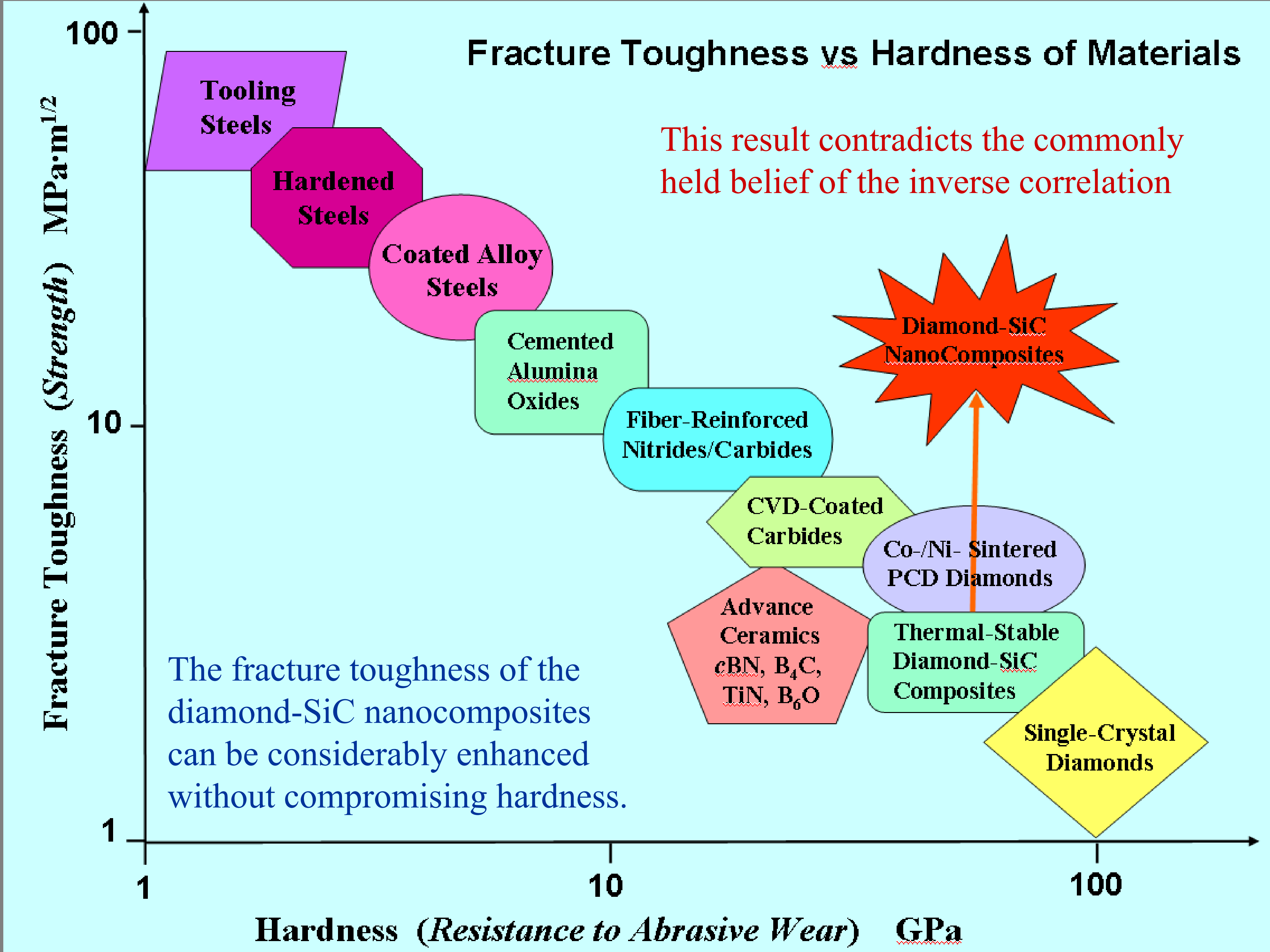
# Novel Superhard Materials and Nanostructured Diamond Composites

## Nanostructued diamond/SiC composites




Granite-log wear resistance of LANL samples compared to a USS standard PDC.

- Wear resistance close to standard PDC
- Much improved impact strength and thermal stability (*toroidal sintering*)


Fracture Toughness vs Hardness of Materials
This result contradicts the commonly held belief of the inverse correlation
Fracture Toughness (Strength) MPa·m^1/2
100
10
1
Tooling Steels
Hardened Steels
Coated Alloy Steels
Cemented Alumina Oxides
Fiber-Reinforced Nitrides/Carbides
CVD-Coated Carbides
Co-/Ni- Sintered PCD Diamonds
Diamond-SiC NanoComposites
Advance Ceramics cBN, B4C, TiN, B6O
Thermal-Stable Diamond-SiC Composites
Single-Crystal Diamonds
The fracture toughness of the diamond-SiC nanocomposites can be considerably enhanced without compromising hardness.
1
10
100
Hardness (Resistance to Abrasive Wear) GPa

# Novel Superhard Materials and Nanostructured Diamond Composites

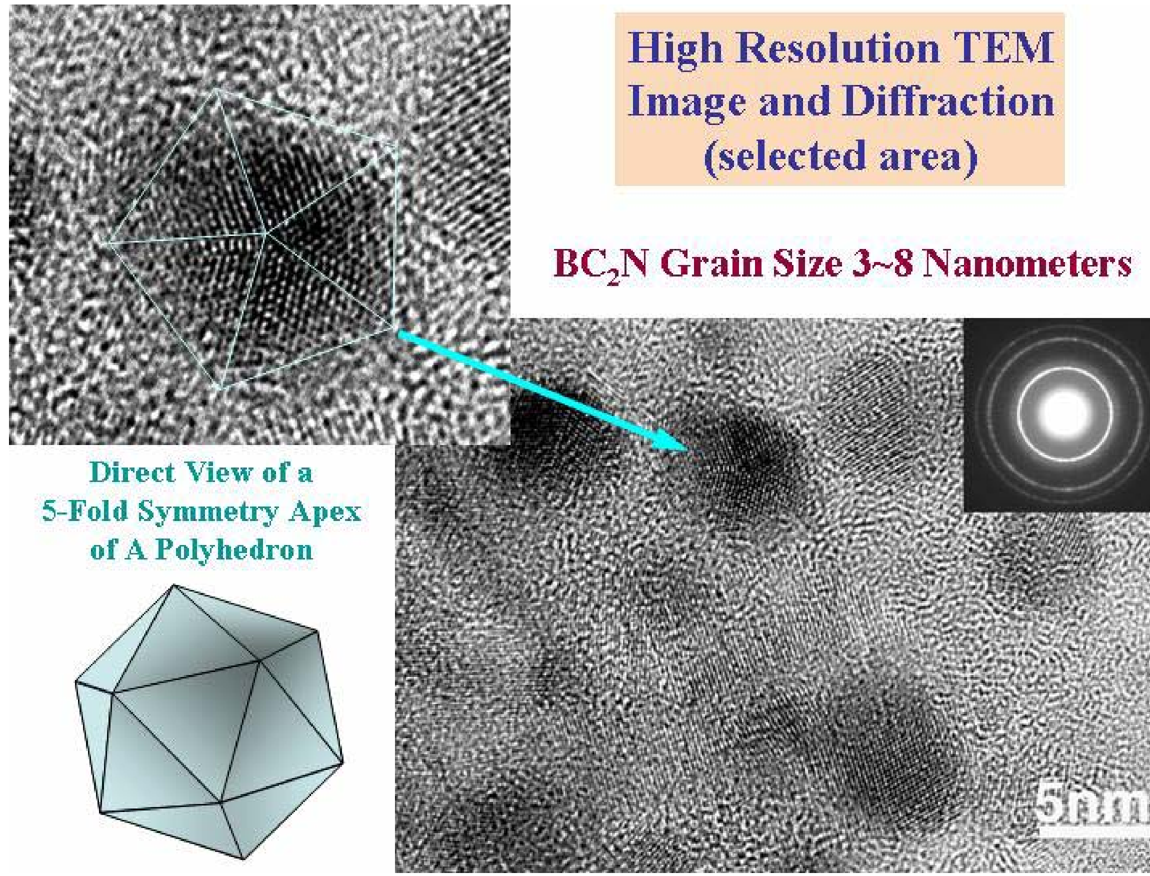
## B-C-N ternary phase

**Starting material:**
- hBN+graphite, HE ball milling
- BN&C amorphous precursor
- nucleus of B-C-N phase

**HP-HT reactive sintering:**
20 GPa, 2200~2500 K

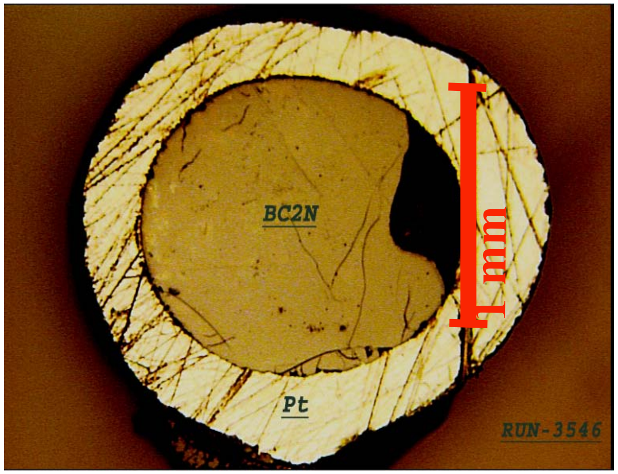
**Final product:**
$BC_2N$, $BC_4N$ ternary phases

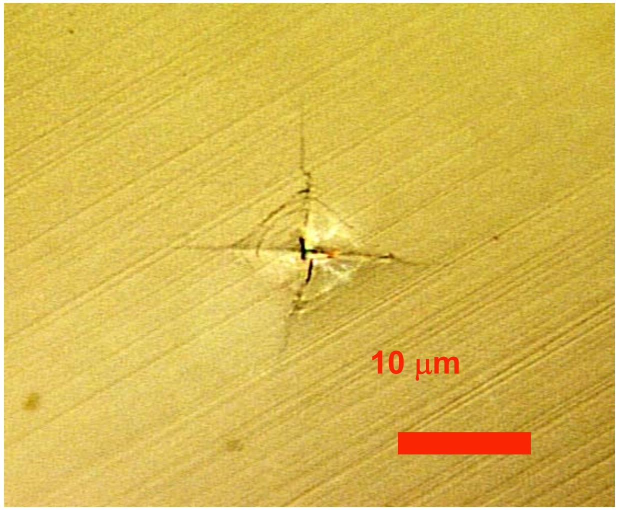
👍 Machining for both ferrous and non-ferrous materials!

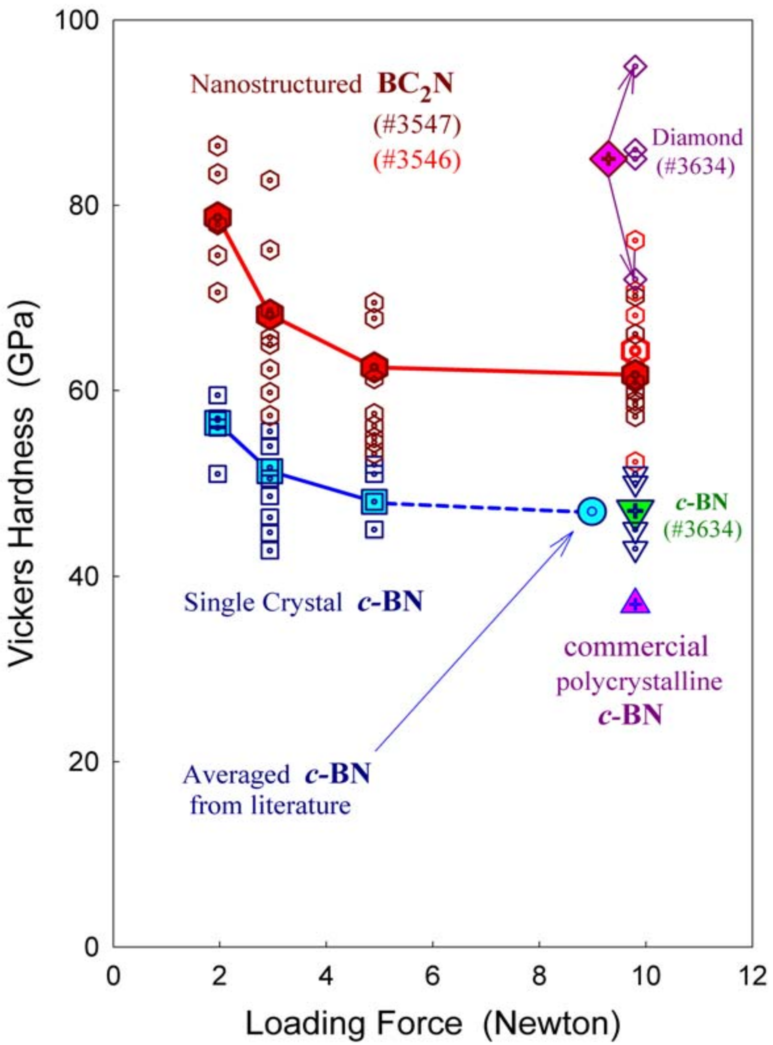


# Novel Superhard Materials and Nanostructured Diamond Composites

## B-C-N ternary phase: 2nd hardest only yield to diamond!



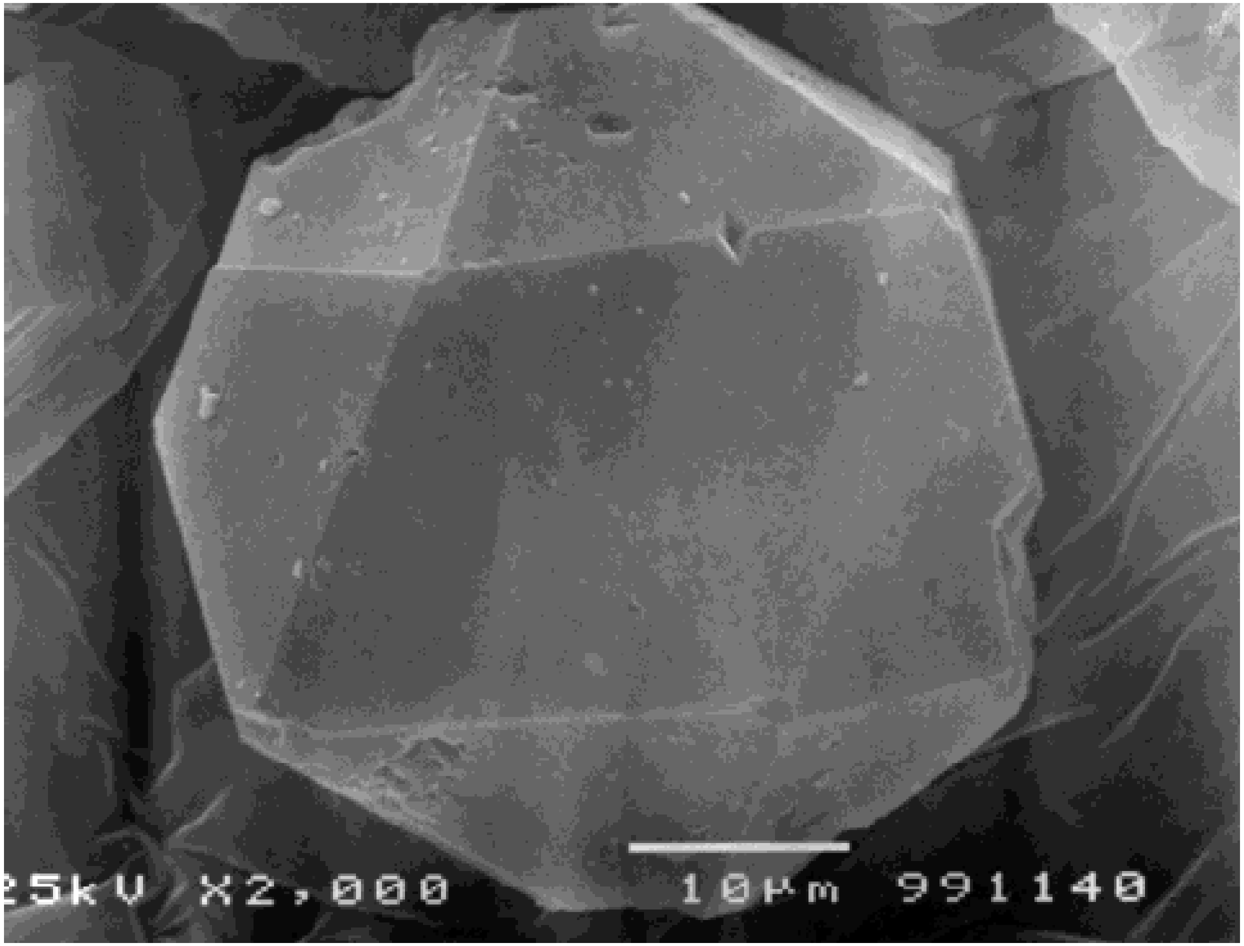



# Boron suboxide ($B_6O$)

**Starting material:**
- B lump in $B_2O_3$ powder
- $B+B_2O_3$ mixture

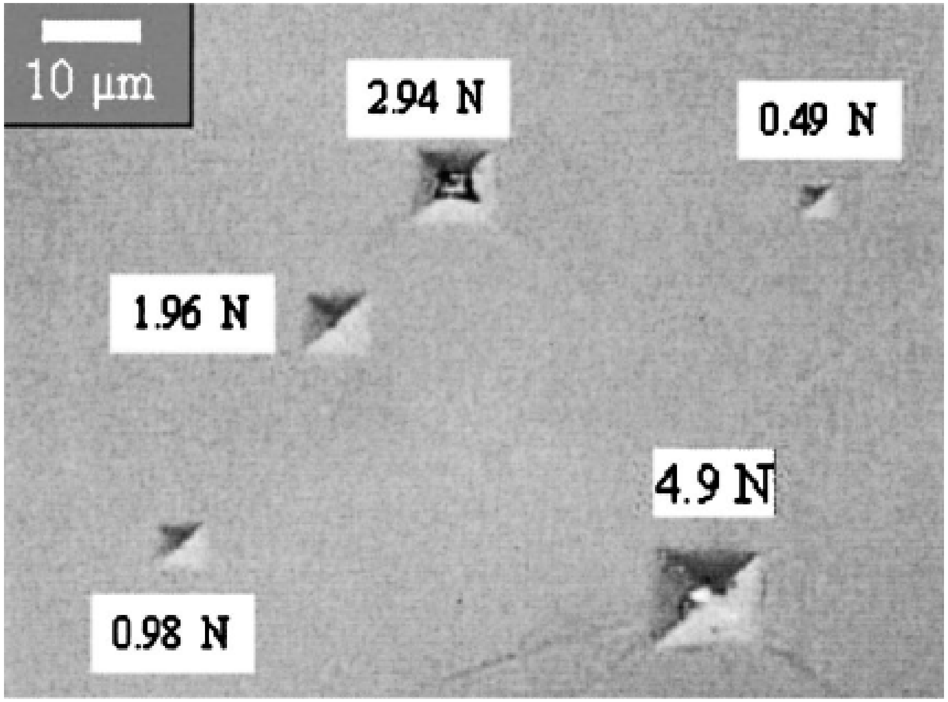
**HP-HT sintering:**
4.5~6.5 GPa,
2000~2500 K

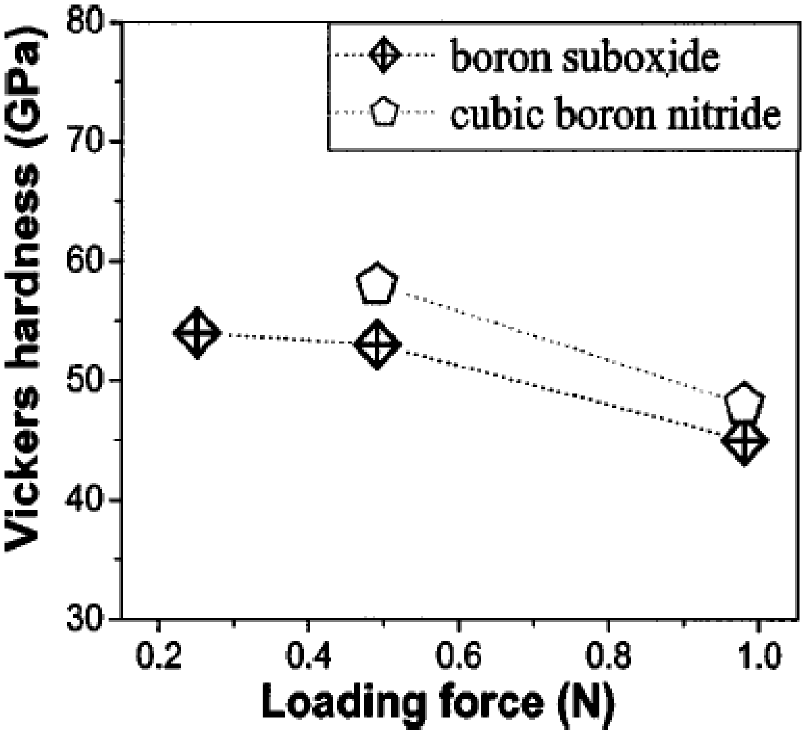
**Final product:**
$B_6O$ single crystal



# Novel Superhard Materials and Nanostructured Diamond Composites

## Boron suboxide ($B_6O$)




As hard as cBN, exceptional thermal stability as oxides!

# Major milestones (FY2002)

| ID# | Milestone description | Planned completion | Actual completion | Comments |
|---|---|---|---|---|
| 1 | B-C-N ternary phase | | | |
| 1.1 | Synthesis BCN, $BC_2N$, and $BC_4N$ | 6/30/02 | 6/30/02 | Done |
| 1.2 | Characterize $BC_2N$ & $BC_4N$ | 9/30/02 | 9/30/02 | Done |
| 1.3 | Publish data on B-C-N | 12/31/02 | 12/31/02 | Done |
| | | | | |
| 2 | Boron suboxide ($B_6O$) | | | |
| 2.1 | Synthesis $B_6O$ crystal | 3/31/02 | 3/31/02 | Done |
| 2.2 | Characterize $B_6O$ crystal | 6/30/02 | 6/30/02 | Done |
| 2.3 | Publish data on $B_6O$ | 9/30/02 | 9/30/02 | Done |

# Major milestones (FY2003 & 2004)

| ID# | Milestone description | Planned completion | Actual completion | Comments |
|---|---|---|---|---|
| 3 | Diamond-SiC nanocomposites | | | |
| 3.1 | Synthesis nano diamond-SiC | 12/31/02 | 12/31/02 | Done |
| 3.2 | Characterize diamond-SiC | 6/30/03 | 6/30/03 | Done |
| 3.3 | Publish data on diamond-SiC | 12/31/03 | 12/31/03 | Done |
| 3.4 | Optimize diamond-SiC synthesis | 3/31/04 | 3/31/04 | Done/on-going |
| 4 | $B_6O$ nanocomposites | | | |
| 4.1 | Synthesis $B_6O$ nanocomposites | 3/31/04 | 3/31/04 | Done |
| 4.2 | Characterize $B_6O$ nanocomposites | 6/30/04 | 6/30/04 | Done |
| 4.3 | Optimize $B_6O$ synthesis conditions | 9/30/04 | 9/30/04 | Done/on-going |
| 4.4 | Publish data on $B_6O$ nanocomposites | 12/31/04 | 12/31/04 | Done |

# Major milestones (FY2004 & 2005)

| ID# | Milestone description | Planned | Actual | Comments |
|---|---|---|---|---|
| 5 | Drill bits with diamond-SiC inserts | | | |
| 5.1 | Massive production of diamond-SiC | 3/31/04 | 3/31/04 | Done |
| 5.2 | Wear test of diamond-SiC with industrial standards | 6/30/04 | 12/31/04 | * **Delayed** |
| 5.3 | Mount/braze diamond-SiC on WC inserts | 9/30/04 | 9/30/04 | Done |
| 5.4 | Impact test of diamond tipped inserts | 12/31/04 | 12/31/04 | Done |
| 5.5 | CTE measurement with ND | 5/31/05 | 5/31/05 | Done |
| 5.6 | RS/S mapping with HE synchrotron x-ray | 9/30/05 | | Beam time obtained |
| 5.7 | Mount diamond tipped inserts on drill bit | 12/30/05 | | In coordination |
| 5.8 | Preliminary field test of drill bit with diamond tipped inserts | 9/30/06 | | |

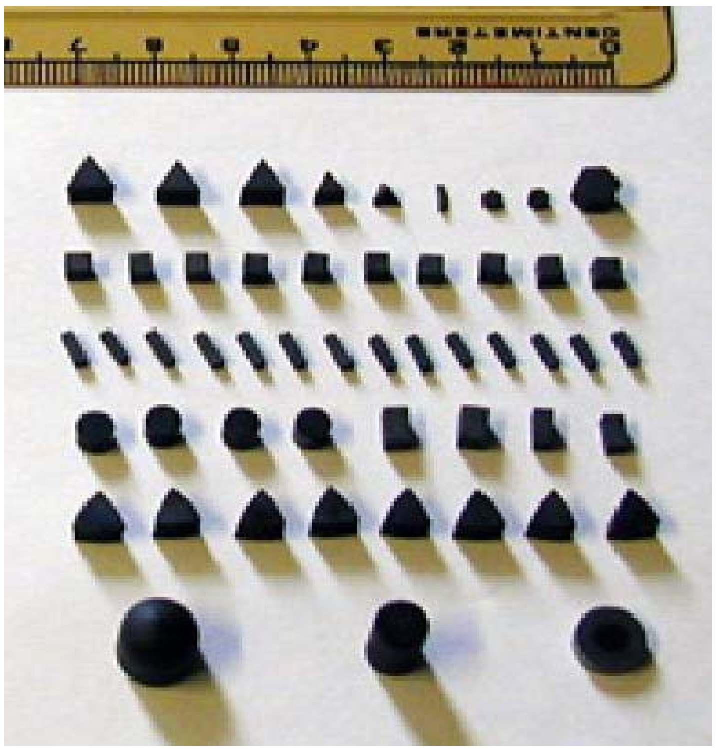
* **Delayed due to the tight schedule of our industrial partner.**

# Major milestones (FY2004 & 2005) continue…

| ID# | Milestone description | Planned completion | Actual completion | Comments |
|---|---|---|---|---|
| 6 | Nano $B_6O$ for machinning tools | | | |
| 6.1 | Bulk production of nano $B_6O$ | 3/31/05 | 3/31/05 | Done |
| 6.2 | Sinter $TiB_2/TiB_4$ bonded nano $B_6O$ | 12/30/05 | | On-going |
| 6.3 | Braze nano $B_6O$ on tool body | 9/30/06 | | |

- 2002 novel superhard materials: B-C-N ternary phase and $B_6O$ crystal.
- 2003 & 2004 nanostructured composites: diamond-SiC and $B_6O$
- 2004 & 2005
  - (1) test of nanostructured diamond-SiC composites with industrial standard
  - (2) fabricate diamond tipped inserts with brazing technology
  - (3) Initial field test of diamond tipped inserts

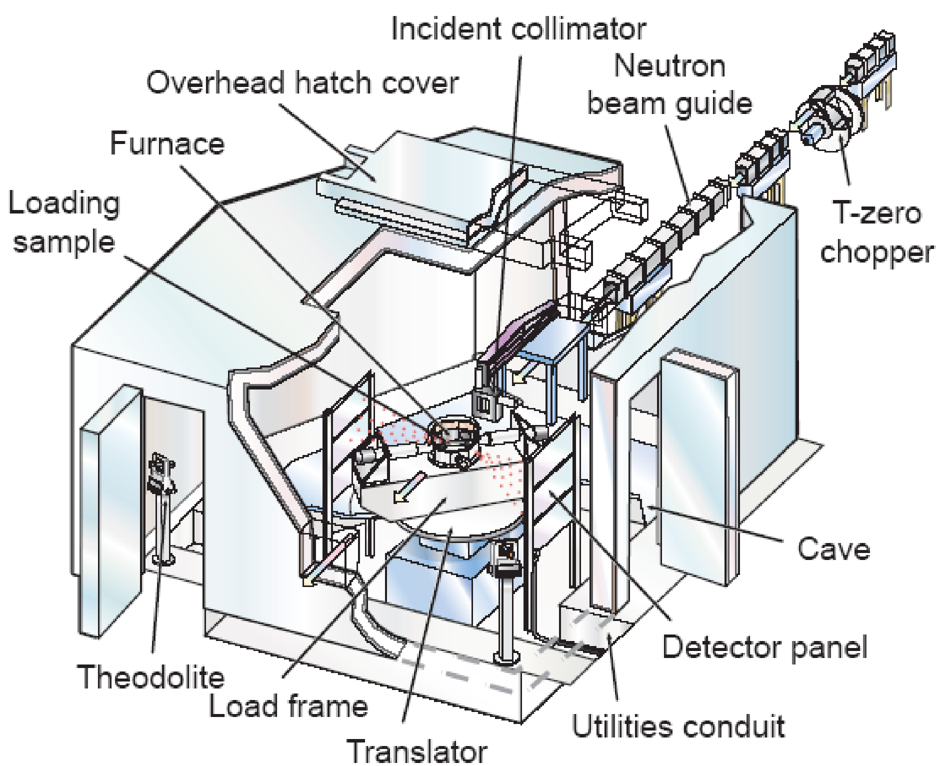
## Highlight of most recent milestones:
## *bulk production and braze diamond-SiC on WC inserts*



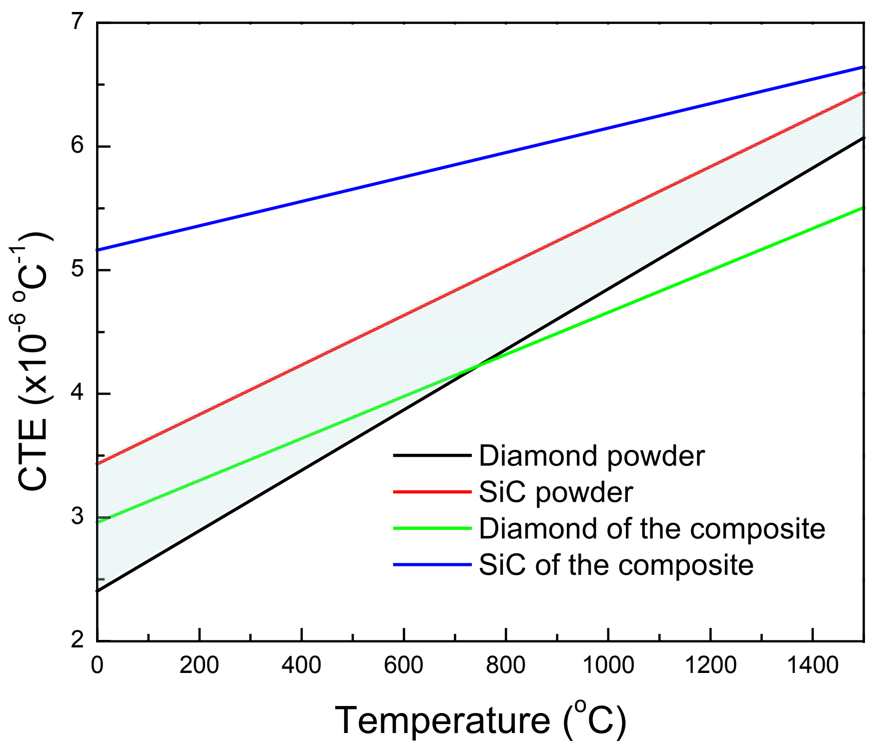
- Standard industrial P-T conditions
- Sample size: 1” dia x 0.5” h

- Vacuum brazing: Ti alloy @ 1150 K
- Strong bonding: TiC

# Highlight of most recent milestones:
## *Thermal expansion study with Neutron Diffraction*




SMARTS Neutron Diffraction:
non-destructive, bulk effect!

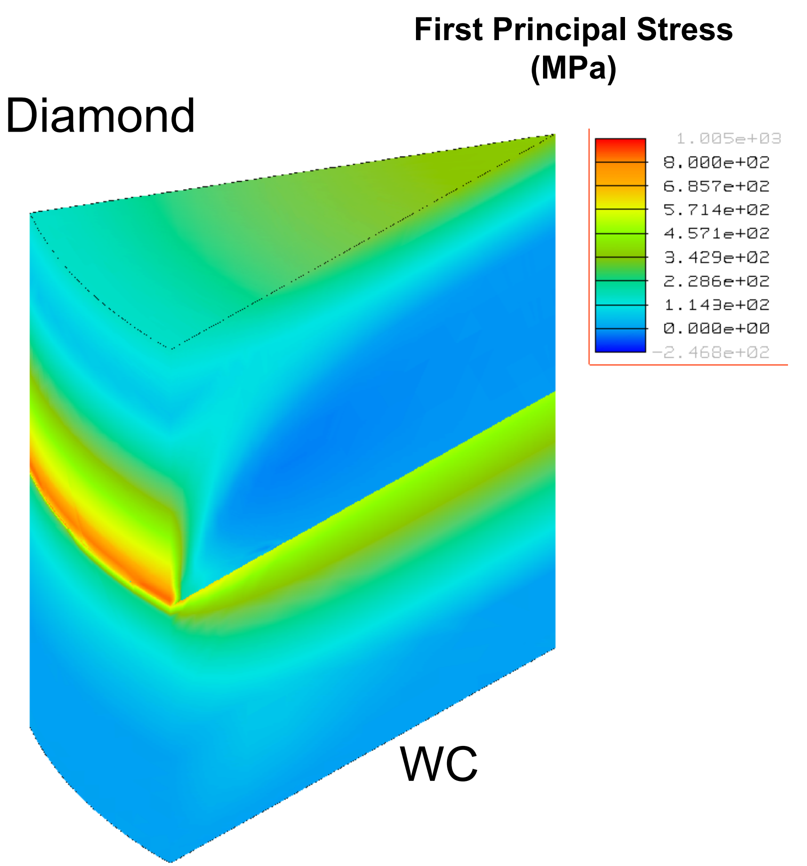



- diamond-SiC stable up to 1800K
- Thermal expansion gap can be further reduced

# Novel Superhard Materials and Nanostructured Diamond Composites

## Highlight of most recent milestones:

*Residual stress/strain study with high-energy synchrotron x-ray*




FEA modeling: tensile stress @ interface

**Residual Stress/Strain:**
***origin for brittle failure!***

High Energy synchrotron x-ray:
- Deep penetration
- 3D mapping of RS/S
- High spatial resolution 100 $\times$100 $\mu m^2$
- Fast data collection

Goal:
- Confirm FEA model
- Realize compressive RS/S
  - different structure design
  - sinter process parameters
  - post sintering treatment

**Beam time scheduled for**
**Aug 25~29@NSLS!!**

# Highlight of recent milestones: $B_6O$ nanocomposites

**$B_6O$ polycrystalline bulks *versus* large single crystals ?!**

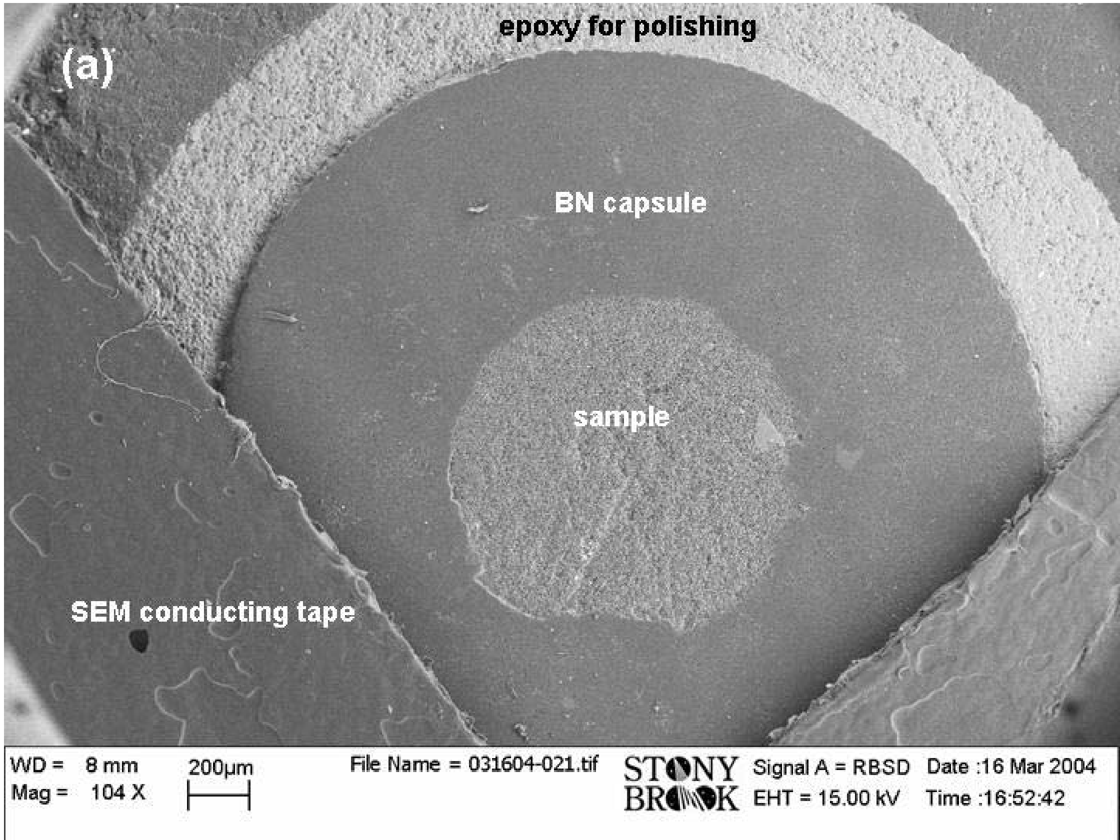
**Starting material:**

- $B+B_2O_3$ mixture, HE ball milling
- Ti doping for TiB bonding

**HP-HT reactive sintering:**
10 GPa, 1800~2200 K

**Final product:**
$B_6O$ nanocomposite

Machining for both ferrous and non-ferrous materials!



# Future plans

**(1) Nanostructured diamond-SiC composites:**

12/31/05 Field test analysis
*3/31/06 Reports on preliminary field test*
go↓
6/30/06 Develop brazing technique
Optimize solvent content
Test induction heating
9/30/06 Standardize impact test
Eliminate redundant impact
12/31/06 Design more diamond tipped inserts
Commercialize thermal stable inserts technology
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**(2) $B_6O$ nanocomposites:**

*3/31/06 Test of $B_6O$ work piece*
go↓
6/30/06 braze $B_6O$ on WC inserts
9/30/06 Impact test $B_6O$ tipped inserts
12/31/06 Amount $B_6O$ tipped inserts on drill bit
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**(3) Nanotube & nanowire reinforced superhard composites**

6/30/06 Wetable carbon nanotube
12/31/06 Tough SiC nanowire
6/30/07 NT & NW reinforced diamond, $B_6O$, and/or B-C-N composites
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# Commercialization

### *Plan*

• License/transfer thermal stable Inserts technology to superhard cutter and drill bit manufacturing Industry.

### *Pathways*

• Functional structure design and starting material preparation at LANL.

• Sintering and test according to industrial standards.

• Our industrial partners have the priority for technology licensing and transfer.

### *Risks*

• Intelligence property issues.

• Communication and information sharing