Available for License

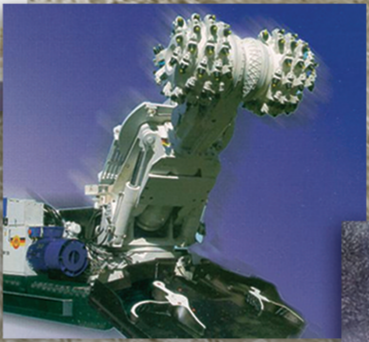
Superhard ULTRATOUGH Nanocomposites

Toughest diamond composites ever produced

Nanoscale structure prevents fracture and promotes wear resistance

Thermally stable to 1200°C

Next-generation abrasive for multiple grinding, cutting, and drilling applications



Los Alamos
NATIONAL LABORATORY

Superhard, Ultratough Nanocomposites

Technology Transfer Contacts
Eric Canuteson
Charlie Gibson
Laura Barber
Email: tmt-2@lanl.gov

Technical Contacts
Jiang Qian
Yushong Zhao

ABOUT THE COVER

The teeth of the roller-cone drilling bit, shown at right, are equipped with abrasive inserts made of our diamond nanocomposites, which stand up to the intense friction, impact, and heat of down-hole drilling environments in the oil and natural-gas industry. Combining superior fracture toughness and thermal stability with the abrasive power of diamond, our nanocomposites can also replace conventional abrasives widely used in many other industries, as suggested by the inset photographs. The improved fracture toughness of our nanocomposites stems from their unique nanoscale structure, which is shown in the highly magnified background image.

Los Alamos
NATIONAL LABORATORY
Los Alamos NM 87545

Executive Summary

Superhard, Ultratough Nanocomposites

Features

Diamond is the material of choice for most abrasive applications because of its superhardness. Unfortunately, its use is limited because diamond is brittle and prone to fracture. We have solved the brittle-fracture problem by developing a novel nanostructured composite that consists of diamond particles embedded in a matrix of nanocrystalline silicon carbide. This nanostructured matrix halts the growth of cracks that lead to fracture. Our nanocomposites are the toughest, most durable diamond composites ever produced. They set a new performance standard for next-generation abrasives. In addition, our innovative synthesis technique can be extended to tailor the properties of other superhard materials.

Applications

Our diamond nanocomposites possess the performance-critical properties required to replace current tungsten carbide and diamond abrasives in a broad range of applications:

- Composite inserts for drilling bits in the oil and gas industry
- Superabrasive components for high-impact mining, grinding, and cutting environments
- High-speed tool surfaces for machining nonferrous alloys and hard ceramics
- High-temperature dies for wire drawing
- Anvils for high-temperature, high-pressure materials research

Benefits

- Fracture resistance and thermal stability combined with the supreme abrasive power of diamond
- Increased drilling, grinding, cutting, and machining speeds
- Extended product life that reduces costly downtime

Overview

An oil-field drilling bit that is hard but not tough will likely shatter when it hits a hard rock formation, while a bit that is tough but not hard will wear out quickly. Regardless of the failure mode, replacing a bit costs significant time and money. In addition to drilling, many industrial processes require materials that are not only hard enough to grind and abrade other materials but also tough enough to resist fracture—a combination that is difficult to find.

Diamond is the material of choice for most applications requiring strong abrasives; it is the hardest material known to man. Unfortunately, its use is limited because diamond is not very tough. It is inherently brittle and prone to fracture because it contains dislocations, intrinsic flaws caused by atomic-level misalignments, which can initiate cracks. Once formed, cracks grow rapidly through diamond because its carbon atoms lack the atomic mobility to dissipate fracture energy through deformation. As a result, diamond succumbs to fracture at stress levels well below its theoretical strength.

We have solved the brittle-fracture problem by combining diamond with nanocrystalline silicon carbide in a new type of composite that exploits the unusually high fracture toughness of nanocrystalline materials. Built up from small atomic clusters with sizes on the order of nanometers (billionths of a meter), nanocrystalline materials can possess fracture strengths approaching theoretical values. The mechanisms responsible for such high strengths are still debated, but it is generally believed that small nanocrystals comprising anywhere from hundreds to thousands of atoms contain few if any dislocations where cracks can be initiated. Further, because growing crack tips are larger than the nanocrystals they encounter, cracks must proceed on a tortuous path over and around nanocrystals in an energy-consuming process that robs them of their driving force.

Our superhard, ultratough nanocomposites consist of a fine-grained matrix of silicon carbide that surrounds individual diamond grains. Silicon carbide is a very hard ceramic compound, although it is not as hard as diamond. It forms strong chemical bonds with diamond surfaces and serves as the “glue” that holds the diamonds together. The majority of diamond grains are several microns (millionths of a meter) in size. Although quite small—there are literally billions of diamond grains within in each cubic centimeter of our composites—the silicon carbide nanocrystals located in between the diamonds are hundreds of times smaller. Cracks originating within diamond grains cannot fracture the composite as a whole because they are defeated by the nanocrystalline silicon carbide matrix, which absorbs cracks and dislocations and endows our nanocomposites with surprising fracture toughness. We believe our nanocomposites are the first example of increased fracture toughness in a bulk composite as a result of the nanoscale fracture-toughening effect of its matrix.

Producing the unique structure of our nanocomposites is a significant technological challenge. The silicon carbide must completely surround the diamond grains to ensure superior mechanical integrity of the composite, and the grain sizes of the silicon carbide must be kept extremely small to exploit the nanoscale fracture-toughening mechanisms.

We have developed a two-step synthesis process that fulfills both of these requirements. First, we mix diamond and silicon powders in a roughly 9-to-1 molar ratio by high-energy ball milling. This process tumbles and pulverizes the powders to produce diamond particles that are uniformly coated by a layer of silicon. Next, we densify the powdered mixture by a process called reactive sintering. It is at this point that silicon carbide forms by the reaction between silicon and carbon at diamond surfaces under high-temperature and high-pressure conditions.

The initial step in this process, high-energy ball milling, is crucial to the formation of the silicon carbide matrix on several counts: (1) Ball milling puts the silicon in intimate contact with all diamond surfaces, so that when silicon carbide forms during reactive sintering, it creates an enveloping matrix around the diamond grains. (2) Ball milling solves the “bottleneck” problem encountered in other techniques for producing diamond/silicon carbide composites, such as liquid infiltration or wet mixing of powders followed by liquid-phase sintering, in which inadequate mixing of diamond and silicon starting materials allows the initial formation of silicon carbide to block molten silicon from reaching all the pores between diamond grains. This leaves residual silicon and porosity trapped within composites, as well as uncoated diamond-grain surfaces, which can transform to graphite during sintering. By developing this ball-milling step, we are able to produce nanocomposites with minimal porosity and no detectable amount of residual silicon or graphite, all of which would negatively impact mechanical properties. (3) Ball milling transforms the initial crystalline structure of the silicon powders into to a low-density amorphous state. At the high pressure of reactive sintering, amorphous silicon promotes the large-scale nucleation of silicon carbide seed crystals that helps produce a fine-grained nanostructured matrix. (4) Ball milling also creates a small amount of nanocrystalline diamond debris that ultimately serves as a strengthening component of the nanostructured matrix.

Controlling the size of silicon carbide nanocrystals as they are being formed during reactive sintering is a delicate balancing act. High temperatures stimulate rapid grain growth that could destroy the nanocrystalline character of the matrix, but high pressures hinder such growth. We balance these factors by a subtle interplay of reaction temperature, pressure, and time, which gives us exquisite control over silicon carbide grain growth. We have found the right combination of these conditions, a “sweet spot” in the parameter space, that leads to the formation of the nanostructured silicon carbide matrix.

We believe that, in addition to the nanoscale-matrix effect, the fracture toughness of our nanocomposites is significantly enhanced by changes to diamond particles during reactive sintering. The carbon/silicon chemical reaction consumes dislocations and other defects concentrated at the surface of diamond particles; additional defects and stresses inside the diamond grains are annealed out at high temperatures and pressures. This “healing” process reduces the likelihood of cracks forming in the diamond grains and propagating through the composite.

Beyond its role as a fracture-toughening agent, silicon carbide is a chemically inert, oxidation-resistant ceramic compound that endows our nanocomposites with thermal stability and mechanical integrity up to 1200°C, well above the working range of pure diamond, which transforms to graphite at 900°C in air. Both diamond and silicon carbide possess high thermal conductivity capable of rapidly dissipating heat, and their similar thermal expansion coefficients reduce the potential of thermal stresses to cause composite failure when exposed to rapid temperature changes and high thermal gradients.

Our superhard, ultratough nanocomposites contradict the commonly held belief that hardness and toughness are inversely related, that improving one property necessarily sacrifices the other. Our nanocomposites exhibit unprecedented fracture toughness without forfeiting diamond’s ability to grind and abrade other materials. This breakthrough combination of properties makes our nanocomposites the new material of choice for a broad range of applications in the drilling, mining, grinding, and machine tooling industries.

To learn more about the innovative synthesis of our nanocomposites and nanoscale fracture-toughening mechanisms, see "Enhancement of Fracture Toughness in Nanostructured Diamond-SiC Composites" in the Appendix.

Competition

Our diamond nanocomposites are unique, combining superior wear resistance and high fracture toughness in a single material. Competing materials possess either one property or the other.

Diacom from Ringwood Superabrasive and Syndax from Element 6—diamond/silicon carbide composites created by liquid-phase sintering of microcrystalline diamond compacts with molten silicon

Diamond Composites from Smith Megadiamond and U.S. Synthetics—diamond/cobalt composites created by melt infiltration of cobalt into a microcrystalline diamond compact mounted on a conventional tungsten carbide/cobalt base

Tungsten carbide composites—conventional tungsten carbide/cobalt composites created by injection molding of tungsten carbide grains bonded by a minor cobalt phase (available from a variety of manufacturers)

Comparison matrix

Parameters	**Superhard, Ultratough Nanocomposites**	**Diamond Composites from Ringwood Superabrasive and Element 6**	**Diamond Composites from Smith Megadiamond and U.S. Synthetics**	**Tungsten Carbide Composites**	**Comments**
Composition	Microcrystalline diamond/nanocrystalline silicon carbide and diamond, no residual silicon or graphite	Microcrystalline diamond/microcrystalline silicon carbide, residual silicon and graphite	Microcrystalline diamond/cobalt	Tungsten carbide/cobalt	Ours is the only product that incorporates a nanostructured phase to bind primary composite particles. The presence of residual silicon, graphite, or metallic cobalt negatively impacts the mechanical properties of competing materials.
Fracture Toughness	12 MPa·m$^{1/2}$	6–9.5 MPa·m$^{1/2}$	6 MPa·m$^{1/2}$	7–10 MPa·m$^{1/2}$	Fracture toughness is indicative of the ability to withstand fracture under high-stress concentration and impact. Our nanocomposites surpass all competitors in terms of fracture toughness.
Hardness	50–80 GPa	40–80 GPa	50–80 GPa	17–24 GPa	Hardness is a measure of abrasive power and wear resistance. The range of values listed for each material is typical of hardness values measured by the Vicker's indentation method.
Thermal Stability	Stable up to 1,200°C	Stable up to 1,200°C	Stable up to 900°C	Stable up to 600°C	The composites lose their mechanical integrity above this temperature. Composites with cobalt as a binding phase have lower working temperatures because the cobalt softens and oxidizes.
Average Drilling Speed (Soft Rock)	150 ft/h	100 ft/h	100 ft/h	N/A	Tungsten carbide is not used to drill soft rock formations because its low hardness translates to low drilling speeds that are not competitive with the diamond-based products. Speeds are based on field tests using drilling bits tipped with the composites to drill a typical 7,000-foot well in eastern Texas.
Average Drilling Speed (Hard Rock)	100 ft/h	N/A	N/A	20 ft/h	Competitors' diamond composites shatter when used to drill hard rock formations. Our nanocomposites can be used to drill quickly and economically through all rock formations. Speeds are based on field tests using drilling bits tipped with the composites to drill a typical 7,000-foot well in eastern Texas.

Advantages

Hardness and fracture toughness in one. Our nanocomposites are the toughest, most durable diamond composites ever produced. They shatter the notion that hardness and toughness are inversely related and set a new standard for abrasive materials. See the Appendix figure, "Fracture Toughness vs. Hardness of Abrasive Materials."

In the past, the relatively high fracture toughness of tungsten carbide–based composites made them a traditional choice for high-stress applications in which fracture is the dominant concern. Our diamond nanocomposites surpass even tungsten carbide in terms of fracture toughness and are over 300% harder, which translates to a 10,000-fold improvement in wear resistance, based on the ratio of weight loss in head-to-head grinding tests.

The superior fracture toughness of our nanocomposites allows the supreme abrasive power of diamond to be brought to bear in high-stress and dynamic-impact environments in which other diamond composites fail.

Improved drilling performance. Down-hole drilling conditions represent one of the most hostile environments encountered by abrasive materials. Drilling bits equipped with abrasive-tipped teeth are designed to scrape, gouge, and break apart geological formations by rotary and vibrational impact. Currently available tungsten carbide and polycrystalline-diamond inserts often do not survive prevailing dynamic impacts and high temperatures caused by friction.

Bits tipped with our diamond nanocomposites are capable of quickly and effectively drilling through sedimentary rock formations where oil and gas deposits are typically trapped, and because of their superior fracture resistance, these drilling bits do not need to be changed when interbedded soft and hard geological formations are encountered; changing bits typically requires 24 to 48 hours downtime.

In field tests conducted by RBI-Gearhart, a leading drilling-bit manufacturer, the effectiveness of our diamond nanocomposites was compared with tungsten carbide and polycrystalline-diamond drilling-bit inserts. The number of bits required to drill a typical 7,000-foot well was reduced from seven to four, the number of down-hole trips required to change bits was reduced from six to three, and overall drilling time was cut by more than half. A letter of endorsement from RBI-Gearhart appears in the Appendix.

Long lasting, thermally stable, and cost-effective abrasives. Blunting, chipping, and shattering of abrasive tools limit their working lifetime for a variety of industrial processes. Reduced operating speeds extend useful tool life but waste significant time and energy. The overall durability of our diamond nanocomposites allows higher operating speeds and increased productivity. Our product lasts longer, which not only saves replacement costs but also downtime—often a controlling economic factor. The high thermal stability of our nanocomposites makes them well suited to dry-machining applications, which eliminate the high costs associated with liquid-coolant use and recycling.

Sensible, flexible processing. The nanostructured matrix that is key to the fracture toughness of our product results from uniform mixing of precursor materials and informed synthesis conditions—rather than expensive new technology. Based on conventional high-pressure, high-temperature techniques and readily available powders, our process is commercially appealing and can produce diamond nanocomposites at competitive prices in a wide range of shapes and sizes. Our technique can be extended to other material systems to design new composites with novel properties.

Our diamond nanocomposites are not an obscure product looking for a niche market. They are the next-generation replacement for tungsten carbide and diamond abrasives currently used in multiple heavy-industrial applications, including natural-resource drilling, hard-rock mining and cutting, construction, and earth moving.

Our diamond nanocomposites can also be employed as machine-tool inserts for high-speed cutting, grinding, and milling of nonferrous alloys as well as difficult-to-machine hard ceramics, for example, silicon nitride and partially stabilized zirconia components used by the automotive and aerospace industries. The thermal and dimensional stability of our product makes it suitable for high-temperature dies used to draw hot metal into wire. The combined hardness and fracture toughness of our diamond nanocomposites make them the material of choice for anvils used in high-temperature, high-pressure materials research.

We expect our product to have its largest single impact in the oil and gas industry, which demands improved drilling technologies to recover oil and gas reserves at deeper and hotter depths, both on land and offshore, to keep pace with increasing energy demands. Our diamond nanocomposites possess the performance-critical properties to meet the challenges of efficient, cost-effective drilling with minimal downtime—an important economic consideration when the rental cost of drilling rigs can range anywhere from \$10,000 to \$100,000 per hour. Downtime costs affect the feasibility of expensive, high-risk offshore drilling operations in particular.

Other applications

We are currently working with the United States Navy to develop superhard nose cones and penetrating rods based on our diamond nanocomposites for deep-penetrating warheads capable of destroying enemy targets buried deep underground. We are also exploring the utility of our product for lightweight, superhard defensive armor.

Summary

Oil and natural gas are the lifeblood of the U.S. economy. Together they account for over 60% of energy consumption and virtually all of our transportation fuels. The Department of Energy predicts that our reliance on these resources will increase for at least the next 20 years. New technologies that reduce the cost of reaching and extracting oil and natural-gas deposits will have an economic impact on every sector of our economy.

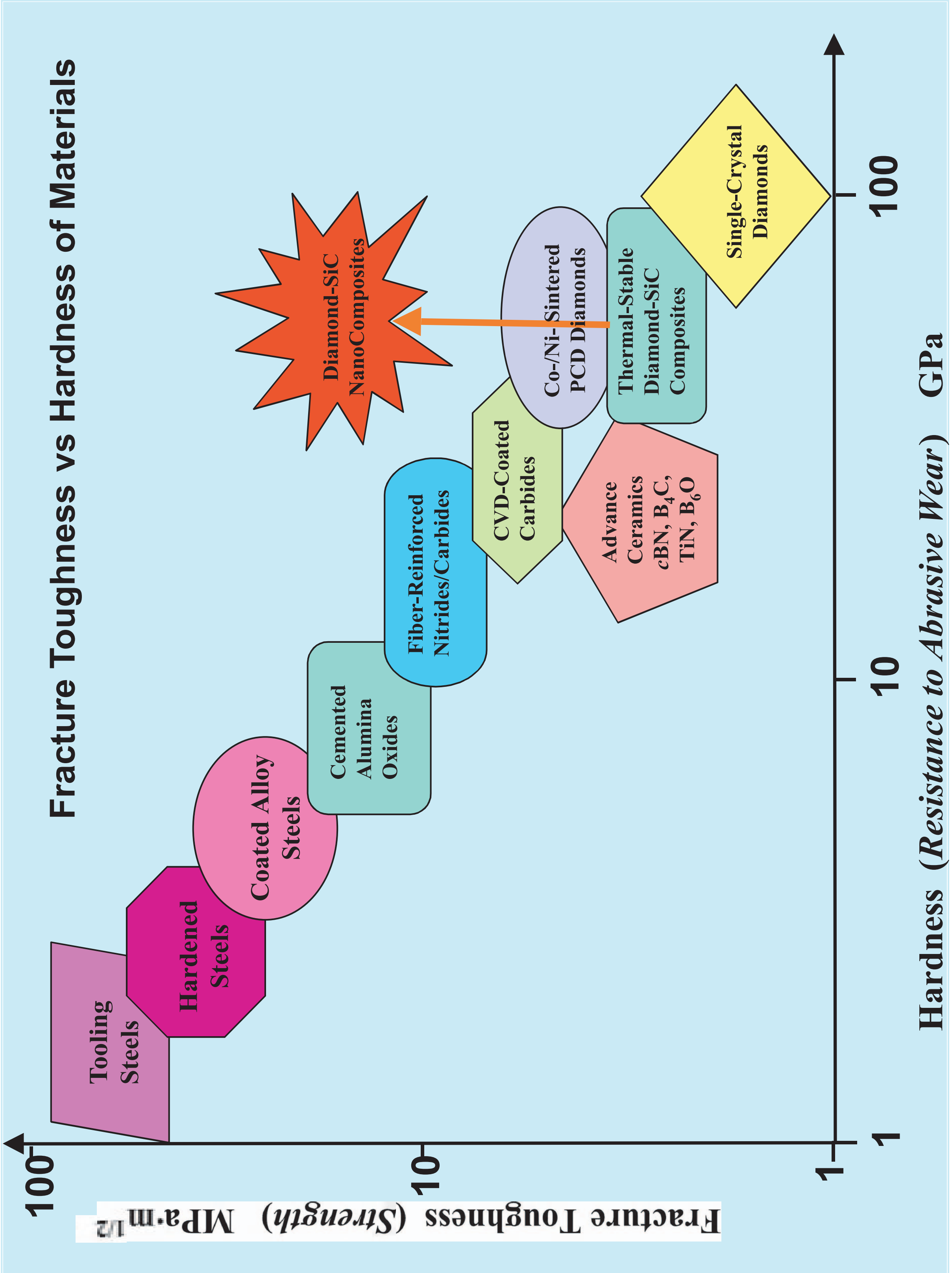
Adopting our diamond nanocomposites for long-lasting and efficient drilling bits will have a major economic impact, simply because of the magnitude of the oil and natural-gas industry. In 2001, there were 34,179 wells drilled in the U.S. with a total footage of nearly 190 million feet. The Gas Research Institute estimates that drilling costs account for 33%–40% of the total finding and developing costs for new gas resources. Drilling oil and gas wells accounts for nearly $10 billion in annual costs to the domestic petroleum industry.

We conservatively estimate $200 million–$500 million in annual savings for the U.S. petroleum industry alone resulting from increased drilling speeds and reduced downtime costs enabled by the use of our product. Of course, drilling for oil and gas is a global enterprise, and along with the worldwide potential of our diamond nanocomposites in other multibillion-dollar mining, cutting, and machining industries, we expect the total economic impact of our product to be significantly larger.

In summary, we have developed a new processing technique to create a novel nanostructured material that solves the long-standing problem of brittle fracture in diamond. Possessing superior fracture toughness and thermal stability combined with the superhardness of diamond, our nanocomposites raise the standard by which abrasives are measured. Nanostructured materials are a new development in the field of superhard materials. Our new synthesis technique, based on high-energy ball milling followed by reactive sintering, is flexible and robust and can be adapted to other material systems to synthesize novel nanostructured materials with properties tailored to specific applications.

Appendix

Figure: Fracture Toughness vs. Hardness of Abrasive Materials



Diamond/SiC nanocomposites break through the usual inverse relationship between hardness and fracture toughness.