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Coating's *Holy Grail*

Commercialization of cubic boron nitride coatings has proven elusive, but a two-step process for coating cutting tools with CBN is expected to come to market 'soon.'

By Alan Richter, Editor

If the hardest known material, diamond, can be coated onto cutting tools, then why isn't CBN, the second hardest material, commercially available as a tool coating? Moreover, why even bother with such coatings when CBN isn't on top of the hardness podium?

The short answer to the latter query is that CBN provides outstanding thermal stability, high abrasive wear resistance and chemical inertness when applied for cutting ferrous alloys, whereas diamond's aggressive reaction with iron at the high temperatures generally reached when machining prevents diamond from being effectively used as a tool material for cutting ferrous alloys.

Answering the first question is a bit more complicated. Nonetheless, Duralor LCC, Springdale, Ark., an offshoot of NanoMech LLC, Fayetteville, Ark., has developed TuffTek CBN-based composite coatings using a technology it licensed from the University of Arkansas-Fayetteville. The technology is reportedly close to commercialization.

CBN Coating Challenges

Research on synthesizing CBN coatings via thermal chemical vapor deposition and plasma-assisted physical vapor deposition (PVD) began in the early 1980s, shortly after pioneering work on CVD diamond coatings showed posi-

itive results, according to Dr. Dennis T. Quinto, a surface engineering consultant with more than a quarter century of experience in cutting tool and coating technologies.

Unlike diamond, CBN doesn't occur naturally, but similar to diamond it can be synthesized into bulk crystalline form, and polycrystalline cubic boron nitride- and PCD-tipped carbide tools are readily available. "The applications for diamond and PCBN tools do not overlap," Quinto said.

In addition, diamond coatings are successfully deposited by CVD and PVD processes, but CBN does not seem amenable to CVD. It can, however, be



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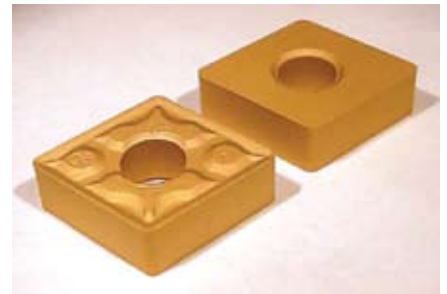
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deposited by plasma-assisted PVD. "As currently known, about 1µm of CBN coating seems to be the maximum coating thickness attainable by researchers—still much too thin for general hard coating functionality," Quinto said.

CBN coating synthesis has proven to be intrinsically more difficult primarily because CBN is composed of two elements: boron and nitrogen. Diamond, on the other hand, is composed of pure carbon. To attain exceptional hardness, the atoms of either material have to be locked into a specific cubic atomic bonding configuration, called sp³, to produce a thermodynamically stable phase, Quinto explained. Otherwise, the atoms might form a hexagonal phase, which is also stable but results in a soft, graphite phase.

According to Quinto, the first requirement in the deposition of coating materials is the nucleation of nanocrystals with the correct bonding configuration and those crystals' subsequent growth into the final crystalline microstructure. The second—and sometimes trickier—requirement for creating a functional tool coating is its adhesion to the underlying substrate. In the CVD process, a tem-



Duralor

Inserts for hard turning applications coated with the TuffTek CBN-based composite coating.

perature of about 1,700° F to 1,850° F creates more atomic mobility, such that atomic rearrangements and long-range order take place easily. This allows nucleation and growth of the nanocrystals into larger crystalline grains.

In lower-temperature PVD (below 950° F), Quinto continued, the atoms tend to be frozen in a relatively short-range order, nucleating much smaller nanocrystals that can hardly grow into crystalline grains. Because the atoms do not always find their "equilibrium positions," a residual stress builds up. "The

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nucleation of CBN seems to be different from that of diamond in that it requires more energy input, or higher ion bombardment, to form the sp^3 bonding configuration," he said. "This is common in PVD hard coatings, but the level of internal stress in CBN coatings seems to be an order of magnitude higher."

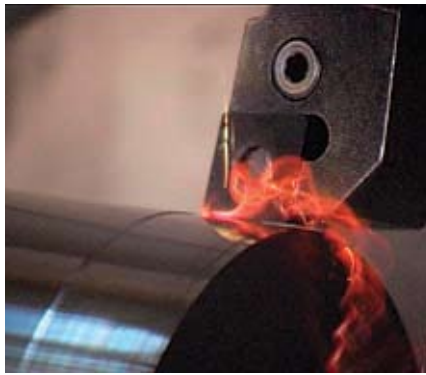
That excessive residual stress has been the main problem in the development of functional CBN coatings. Quinto noted that if the residual stress buildup is not properly accommodated at the coating/substrate interface, the coating will delaminate spontaneously as the thickness of the deposited coating increases. "Residual stresses in PVD coatings are compressive and, when controlled, beneficial in stopping the initiation and propagation of cracks during metalcutting," he said.

To mitigate the impact of excessive residual stress, Quinto added that researchers have attempted to design an interlayer between the coating and substrate. Another approach is to anneal out the stress through an additional step in the coating process. "However, nothing close to the successful adhesion technologies developed with CVD diamond coatings has been attained yet," Quinto noted.

The type of substrate being coated affects how well the CBN coating will adhere, with better adhesion when the substrate's material properties are close to those of the coating. Why not, then, coat CBN onto a PCBN substrate? "That might yield great adhesion, but you lose out on the overall composite properties desired, such as toughness of the tool substrate with superhardness of the coating," Quinto said. Also, such a tool would likely not be economical to produce.

However, PVD-coated PCBN tools are commercially available. According to William Russell, technical program manager for Diamond Innovations, Worthington, Ohio, a coating on PCBN can provide a small measure of friction reduction and oxidation resistance. "CBN has a hard time handling heat," he said. "That's a challenge." Although CBN provides outstanding thermal stability, PCBN's binder chemistry makes it more susceptible to oxidation.

Work continues on depositing CBN films onto tools from the gas phase (see



Fraunhofer Institute for Surface Engineering and Thin Films

A CBN-coated tool in a turning operation.

sidebar on page 52), but significant drawbacks exist for transferring most techniques to industrial applications. "I believe the tool companies have abandoned this approach to CBN coating development and have turned their attention to other new PVD hard coatings instead," Quinto said.

CBN-Based Composite Coatings

Because of the difficulties in depositing CBN coatings by CVD and PVD processes, Dr. Ajay Malshe, chief technology officer for NanoMech, and his

colleagues at the University of Arkansas' Materials and Manufacturing Research Laboratories took a nontraditional approach. That approach involves a two-step process consisting of electrostatic spray coating (ESC) of CBN particles followed by chemical vapor deposition of TiN, TiCN, TiC, hafnium nitride or other traditional coating materials.

"Why can't we take off-the-shelf CBN particulates and see if we can make a coating from that?" Malshe asked. "That's where the breakthrough occurred. The breakthrough is we can deposit cubic boron nitride."

Duralor, which recently became the first tenant at the Springdale (Ark.) Technology Park, is beta testing the technology. "We will have some limited commercialization toward the end of this year or early next year," said Bob Reed, Duralor's chief operating officer. "In a year from now, we're going to be working with large companies."

Working with presynthesized CBN particulates, a green part is created with a coating of CBN particulates up to 1µm via ESC to hold them in place with the

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relatively weak electrostatic forces. "The finer the particles, the better because they had to conform to a magnetic field, and if they were too heavy they couldn't do that," Russell said. He previously worked at Madison Heights, Mich.-based Valenite LLC and assisted the University of Arkansas in infiltrating the thin film of CBN particles with a CVD film to adhere them in the composite coating's matrix, which is the second step of the process.

In that step, a second chemistry, such as TiN, binds those particulates together and to the substrate using chemical vapor infiltration, which is analogous to CVD. The composite coating has a CBN content of 40 to 45 percent by volume. According to Malshe, both the ESC and CVD processes are robust, reproducible and scalable, which are important characteristics for commercialization.

The technology is capable of depositing coatings up to 100µm or thicker, but Reed said the coating is typically less than 20µm thick for the applications being targeted. Those applications

primarily focus on finish hard turning. "We can't focus on everything at the same time," he said.

In a test comparing a TuffTek-coated CNMG 432 insert against PVD TiAlN-coated CNMG 432 inserts, the Tuff-

Both the ESC and CVD processes are robust, reproducible and scalable, which are important characteristics for commercialization.

Tek-coated tool outperformed the "best available" TiAlN-coated insert by 300 percent when turning an AISI 4340 steel shaft hardened to 50 to 52 HRC, according to Duralor. The cut was straight and done with coolant at a cutting speed of 150 m/min. (492 sfm), a feed of 0.15 mm/rev. (0.006 ipr) and a DOC of 0.25mm (0.01").

In another test turning a compressor shaft made of A-2 steel hardened to 58 HRC, Duralor reported that its CBN coating was able to semifinish nine shafts while retaining good cutting edges compared to three shafts for TiAlN-coated inserts, and cycle time was reduced by 50 percent. The cutting speed was 300 sfm, the feed was 0.0043 ipr and the DOC was 0.014". All turning was continuous. "We believe, in time, we'll have product capable of doing interrupted cutting as well," Reed said.

When compared to a PCBN-tipped insert, an insert coated with a CBN-TiN composite coating had about half the tool life when dry turning AISI 4340 steel hardened to 50 to 52 HRC at a cutting speed of 100 m/min., a DOC of 0.5mm and a feed of 0.2 mm/rev., according to a 2006 paper by Malshe and others. "We're not looking to compete with PCBN," Malshe noted.

Along with having flexibility in selecting the second chemistry to bind the CBN particulates, the CBN-based composite coating technology com-



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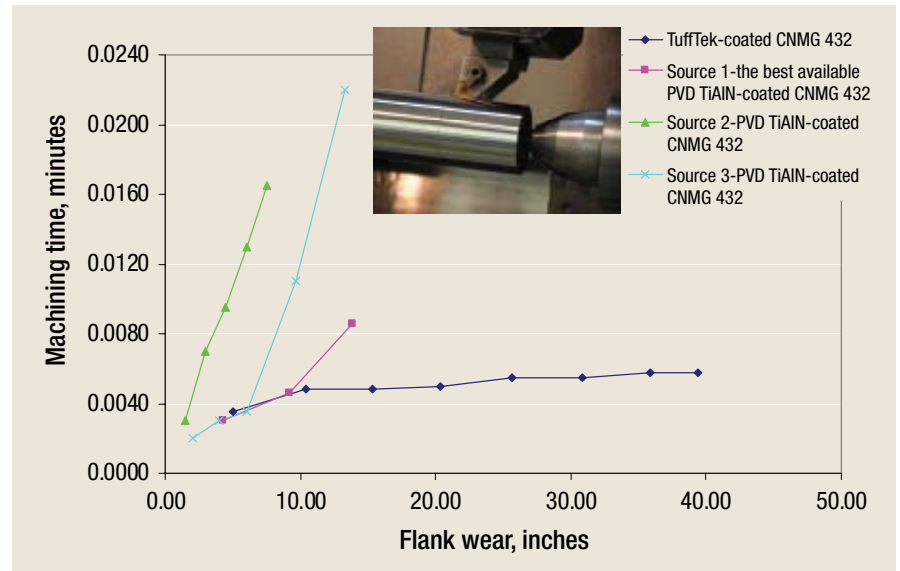
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bin nanostructured and microstructured coatings to provide the ability to tailor each coating's specific structure to the application.

Coating vs. Compact

There are several advantages to applying a CBN coating to a tool substrate compared to brazing a PCBN compact onto a tool. Reed noted that it's possible for a brazed PCBN segment to become loose or separated from the tool it's brazed onto. Malshe added that the brazed bit also might experience chipping. "But in our case, so far we haven't had any challenges in terms of delamination or chipping," he said.

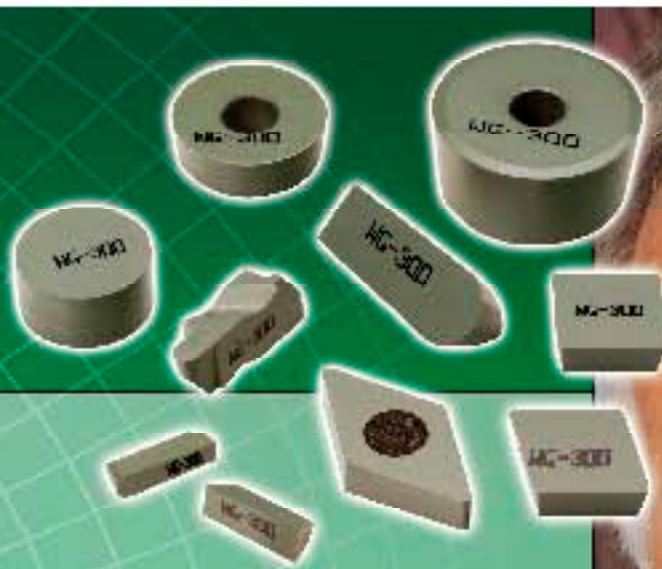
Similar to PCD that's tipped onto a tool, CBN crystals are sintered with binders that are not as hard as CBN to produce PCBN, which reduce the CBN content to about 50 to 90 percent or more, depending on the application it's tailored for, Quinto said. Diamond coatings, on the other hand, are 100 percent diamond. "As long as excellent diamond coating adhesion is achieved—and there



Comparison of flank wear over time of various coated inserts when turning in a straight cut an AISI 4340 steel shaft hardened to 50 to 52 HRC. The cutting speed was 150 m/min., the feed rate was 0.15 mm/rev. and the DOC was 0.25mm. Cutting fluid was applied.

are several technologies that have made this possible on carbide substrates—the diamond-coated tool often outperforms the PCD-tipped tool in metalcutting," he said.

Although the TuffTek coating incorporates a binder, Malshe said the CBN-based composite coating is as hard as PCBN in the particulate form. "The ability to cut material remains the same."



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In addition, Reed said the CBN coating can be applied onto existing chipbreaker geometry to provide chip control. “Chips that don’t break up have typically been a problem with PCBN,” he said.

Although it’s possible to laser machine chipbreakers into PCBN and PCD, the process can be cost prohibitive and the types of geometries are limited to simple

shapes, according to Russell. He noted that virtually any complex shape can be pressed into, say, a carbide insert in its green state before sintering, but doing that subsequently into superhard materials is inherently difficult.

Another similar coating advantage over a tipped insert is the ability of the coating to maintain the cutting edge’s microgeometry, or edge preparation. According

to Quinto, superhard-material tips typically have a flat shape because it’s not feasible to create an edge-hone radius, which is generally done by fine grinding for carbide tools. “Typically, the smallest edge-hone radius on carbide tools is about 10 microns,” he said, adding that a coating’s thickness increases the hone radius. “This means that for fine finishing tools, the coating thickness may be as low

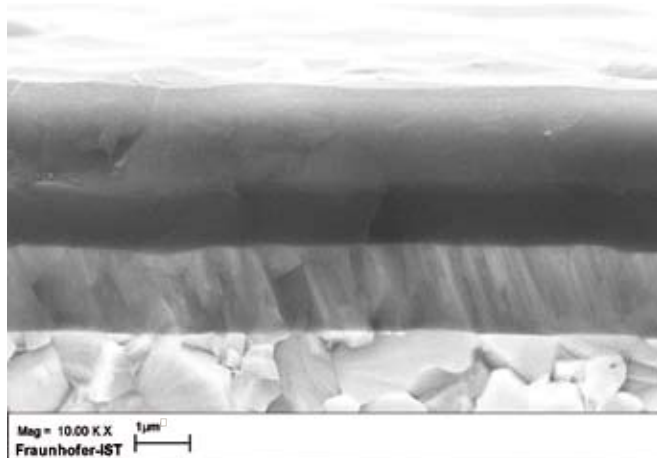
The quest for thick

WITH THE EXCEPTION OF DURALOR’S TuffTek CBN-based composite coating, the deposition of CBN coatings on cutting tools with PVD or plasma-assisted CVD (PACVD) techniques appears to remain a research topic. “We are able to coat cutting inserts with relatively simple shapes, but only prototype coatings at a laboratory scale are possible,” said Dr. Martin Keunecke, Department of New Tribological Coatings, Fraunhofer Institute for Surface Engineering and Thin Films (IST), Braunschweig, Germany, about the institute’s work in depositing CBN coatings thicker than $1\mu\text{m}$.

Generally, all PVD CBN coatings have nanometer-size CBN grains and have high compressive stress. “These high-stress values in combination with sensitivity of such coatings against humidity normally leads to a lack of adhesion and no long-term stability,” Keunecke said. He added that PACVD techniques could deposit larger grains, but those techniques require relatively high temperatures—carbide’s enemy—and utilize fluorine chemistry with hydrofluoric acid. The high chemical reactivity of the fluorine species means that nearly every material in the reactor, particularly steel vacuum chambers and components such as flanges, will be negatively impacted. Therefore, the process is difficult to upscale to industrial dimensions.

To improve adhesion and stability, IST precoats a carbide insert with TiAlN in a thickness from $2\mu\text{m}$ to $2.5\mu\text{m}$ to act as an adhesion layer via reactive DC magnetron sputtering in unbalanced mode and then deposits a CBN layer system. That layer system starts with an approximately $1\mu\text{m}$ -thick boron carbide (B_4C) layer deposited in a pure argon atmosphere followed by a $0.1\mu\text{m}$ to $0.2\mu\text{m}$ B-C-N gradient layer and CBN nucleation layer by incrementally exchanging the sputter gas from argon to an argon/nitrogen mixture. The incremental exchange of gases leads to a gradual transition from B_4C to CBN. Those layers are then topped with a $1\mu\text{m}$ to $2\mu\text{m}$ CBN layer in a pure nitrogen atmosphere. Keunecke said all layers in the CBN layer system contain carbon, which helps stabilize the system. “Our approach to obtaining thicker CBN films leads to an improvement of adhesion and a mechanical stabilization of the CBN layer system without an essential stress reduction.”

The CBN layer system is deposited via a radio frequency (13.56 MHz) diode reactive sputtering unit, but the conductivity of boron carbide is sufficient for use as a target material in a DC sputtering process, Keunecke noted. Reactive sputtering means that a significant portion of the coating is introduced by a gas, such as TiAlN’s nitrogen, to the sputtering atmosphere.



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A scanning electron microscope cross section showing a cemented carbide substrate coated with TiAlN, a boron-carbide layer, an approximate $0.1\mu\text{m}$ to $0.2\mu\text{m}$ B-C-N gradient layer and an approximate $2\mu\text{m}$ CBN top layer. (The gradient layer is not visible in this magnification.)

The hardness of CBN on cutting tools is about 5,100 HV when measured using a Fischerscope device with a Vickers indenter. That compares to 2,400 HV for TiAlN.

IST, in cooperation with IWF, TU Berlin, another research institute, conducted dry external cylindrical turning tests with a CNMA 120408 insert cutting H-13 steel hardened to 52 HRC at cutting speeds from 60 to 100 m/min., a feed of 0.1 mm/rev. and a DOC of 0.5mm. IST reported that: “The difference in performance is significant even with higher cutting speeds and leads to more than double the tool life of the CBN layer system compared to only TiAlN coatings. But we also have to recognize that after a certain cutting time, the width of the flank wear land increases very fast. This behavior could imply that the superhard CBN layer is mostly used up. This means that for a further increase in tool performance, the thickness of the CBN portion in the coating system should be increased.”

Compared to a commercially available PCBN compact, Keunecke indicated that the coating with TiAlN, B_4C , B-C-N and CBN achieved up to approximately 80 percent of the tool life.

If the technology can be scaled to industrially relevant deposition processes and transferred to industrial cutting tool applications, IST could license the process. “If we can synthesize a CBN coating with a comparable cutting performance to PCBN, it would reduce tool costs significantly even if the coating process is quite complex,” Keunecke said.

—A. Richter

as 2 to 3 microns to maintain edge sharpness. It has been theoretically calculated that PVD coating residual stress would cause coating delamination if the edge radius is too sharp, such as smaller than 10 microns. Of course, this would be even worse for a highly stressed coating such as CBN." Quinto added that the hone radius for carbide cutting edges is usually from 25µm to 50µm and the PVD coating thickness is from 4µm to 8µm.

When industrial production of CBN-coated cutting tools will start exactly isn't certain, but when it does the market for them should be sizeable. Quinto indicated that the annual global market for PCBN tools is about \$443 million, with U.S. sales accounting for about 20 percent. "CBN-coated tools would compete against existing PCBN tools," he said. Quinto added that PCBN-tipped inserts

are five to 10 times the cost of CVD- and PVD-coated inserts, but as the price for the superhard tools goes down, the market penetration increases.

Reed didn't offer specific data for the demand for the holy grail of tool coatings—only his gut instinct. "I think the size of the market is really huge," he said. "This has applications all over the place."

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