As Hard as Diamond?

Tracking the elusive carbon nitride

By CORINNA WU

The clear, brilliant sparkle of diamonds makes them the most sought-after gemstones in the world. Beyond the romance and mystery that they evoke, diamonds also have mundane, yet important, industrial purposes. Their extraordinary hardness makes them essential for slicing and polishing other hard materials and increasing the durability of manufacturing tools.

That's why in the late 1980s, when physicists at the University of California, Berkeley announced that they had designed a material predicted to rival the hardness of diamond, a flash of excitement spread among researchers around the world.

In subsequent years, several groups claimed to have synthesized this form of carbon nitride, known as β-C_3N_4. Unfortunately, they had spoken too soon. Today, there's "general agreement that no one has really made it yet," says Robert C. DeVries, an independent consultant from Burnt Hills, N.Y., who retired from General Electric Research Laboratories.

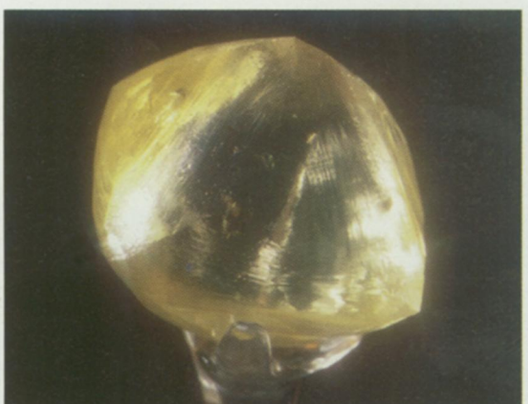
"I don't think we had a clue at the time that it would be so difficult," says Yip-Wah Chung of Northwestern University in Evanston, Ill., one of the materials scientists who attempted the synthesis. "Trying to beat diamond—it was like being able to travel faster than the speed of light. There was this mystique that it would be great to overcome that physical barrier.

"Now," he continues, "people are more realistic, but we are also seeing all these spin-off ideas and applications that we didn't think about before."

Superhard carbon nitride, however, may have already made an appearance in an unexpected form. While scientists still don't have any chunks of the material, preliminary evidence suggests that β-C_3N_4 can form in very thin layers, sandwiched between other materials. These new composites may offer scientists their best chance of glimpsing this rare structure.

Looking at a diamond, it's difficult to believe that it's made of the same material found in graphite pencil leads and in crumbly lumps of coal. In a diamond, the carbon atoms arrange themselves in a rigid crystal structure, whereas in graphite, the atoms form slippery, flat sheets.

In 1955, scientists at General Electric successfully created the first synthetic diamonds by subjecting graphite to very high pressure. The diamonds produced this way are tiny, like sand grains, so they find their best uses industrially as abrasives.



Strength and beauty: An uncut diamond weighs-in at 253.7 carats.

Researchers also tried to squeeze a form of carbon nitride that resembles graphite. They had hoped to get carbon nitride crystals, which they expected to be a new hard material, but they invariably ended up with diamonds, says David M. Teter of Virginia Tech in Blacksburg.

Diamond, despite its utility, is not the universal cutting tool. It doesn't slice steel very well, for instance. Steel itself is primarily a mixture of iron and carbon, and at high temperatures, "iron acts like a sponge for carbon," says Chung. When a diamond-tipped tool is rubbed against a piece of steel, "eventually, the diamond self-destructs." Diamonds end up being useful only for 15 percent of industrial metal-cutting applications, Chung adds.

Researchers, therefore, are on the lookout for other hard, industrially useful materials. The runner-up in terms of hardness is cubic boron nitride, which is only half as hard as diamond. Most steel-cutting tools use more practical materials called cemented carbides, such as composites of tungsten carbide and cobalt.

In the 1980s, researchers developed powerful theoretical tools that could predict properties of materials. These methods renewed excitement about creating superhard substances. In 1985, Marvin L. Cohen of the University of California, Berkeley found a simple relationship between the length of bonds connecting atoms in a material and its bulk modulus, a measure of how well a material resists compression. "You could [use] a hand calculator and get results as good as a supercomputer," he says.

Cohen and his Berkeley colleague Amy Liu began using the formula to predict the bulk moduli of materials. In 1989, they announced that a particular crystalline arrangement of carbon and nitrogen atoms—not found in nature—would approach the hardness of diamond. This structure, β-C_3N_4, probably represents the earliest attempt to develop a superior material from quantum mechanics, says Gerbrand Ceder of the Massachusetts Institute of Technology in the May 15 SCIENCE.

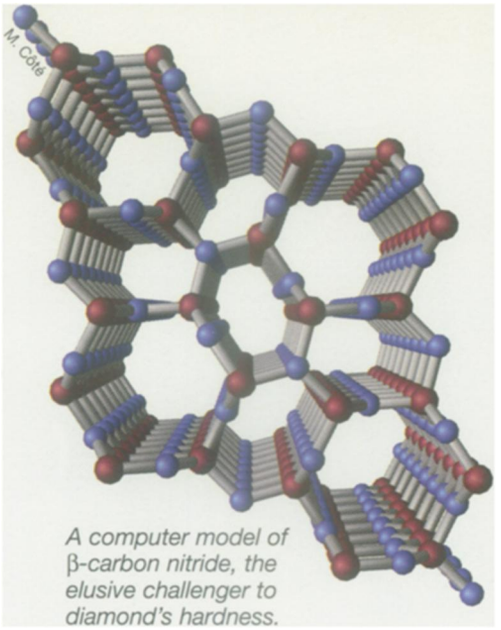
"These calculations have reached a point where, if you put in any element and crystal structure and optimize it, you can calculate properties with incredible accuracy," says Teter.

Although β-C_3N_4 existed only on paper, the report sparked a flurry of activity by groups all over the world.

Chung and his colleagues started attempting to synthesize β-C_3N_4 in 1991. "We tried the obvious thing and used the method called sputtering," in which argon is used to blast carbon atoms off of a piece of graphite in an atmosphere of nitrogen. "The idea at the time was that if you can somehow mix carbon and nitrogen together, maybe we'll let Mother Nature take its course and form this carbon nitride material." But that approach didn't succeed.

One of the most notable examples of a false sighting was a work published in the July 16, 1993 SCIENCE by a group at Harvard University. Also that year, Cohen and his colleagues Eugene Haller and William Hansen received a patent for the material, although other researchers doubt that the team actually made any β-C_3N_4. Later, yet other groups who claimed success also failed to convince observers that they had created the substance.

Cohen says that although Haller had enough material to do microscopy, "it gets very controversial at those small amounts. Up to this point, no one has shown me a



A computer model of β-carbon nitride, the elusive challenger to diamond's hardness.

nice piece of carbon nitride."

In the Jan. 5, 1996 SCIENCE, Teter and Russell J. Hemley of the Geophysical Laboratory of the Carnegie Institution of Washington, D.C., reported calculations indicating that another form of carbon nitride, α-C_3N_4, would probably be more stable and harder than the β-form. The bulk modulus of α-C_3N_4 should be 10 percent higher than diamond, they predicted.

DeVries, in a December 1997 MATERIALS RESEARCH INNOVATIONS review, counted more than 400 studies on carbon nitride. Sixty-five claimed the synthesis of β-C_3N_4, 15 were skeptical of its synthesis, and about 249 reported synthesizing other types of carbon nitride. At least another hundred studies on carbon nitrides have come out since his review, DeVries says.

"Five hundred papers and no one has made anything," grumbles Rustum Roy, a materials scientist at the Pennsylvania State University in State College. "It's been a tragic waste of time."

To create β-C_3N_4, some groups have tried allowing carbon and nitrogen to react under high pressure in a diamond anvil cell. That approach looks interesting, says DeVries, but "the problem with C_3N_4 may be that, even if it exists, it may be difficult to bring back alive." Once the pressure is released, it seems to disintegrate—not helpful from a practical point of view.

Although physicists discuss a material's hardness in terms of characteristics such as its bulk modulus, engineers often measure it experimentally by indenting the surface with a diamond tip. On this scale, diamond's hardness is around 100 gigapascals (GPa) of pressure, while cubic boron nitride has a hardness of 50 GPa. The hardness of steel is only about 3 GPa.

According to Teter, there simply may not be a material that can rival the hardness of diamond. He argues that equating hardness with bulk modulus is not necessarily the best guide to a material's behavior in practical applications.

Physicist Neil W. Ashcroft of Cornell University suggested to Teter a few years ago that another property called shear modulus may be more useful. The shear modulus indicates how well a material resists a tearing force, like the force generated by rubbing two palms together. Aluminum, for example, has a fairly large bulk modulus but is not considered a hard material because its shear modulus is small.

Teter investigated the correlations between the different values while doing research with Hemley at the Carnegie Institution. During one particularly snowy Washington, D.C., winter, he passed the time analyzing and correlating hardness data with bulk modulus and shear modulus values, he recalls. He assembled more than a thousand measurements and found that shear modulus indeed predicts hardness better than bulk modulus. Diamond has the highest shear modulus as well as the highest bulk modulus of any known material.

The predicted shear modulus of carbon nitride is only 60 percent that of diamond, says Teter, "so even if you did make it, this material would not be harder than diamond." Teter reported his findings in the January MRS BULLETIN, a publication of the Materials Research Society. Researchers may have been looking for the wrong material all along, he says.

Materials scientists can argue over how much each parameter contributes to the measured hardness, says Cohen, but connecting theory with experiment is "a very difficult problem. We looked at shear modulus too, but you get into a can of worms."

Other factors further complicate the analysis. For example, the diamond indenter itself affects the hardness by creating defects in the material, Cohen says.

Despite the failure to synthesize chunks of β-C_3N_4, researchers have produced some useful materials along the way. Many groups made an amorphous form of carbon nitride that didn't have the rigid structure they were hoping for. "The hardness [25 to 30 GPa] wasn't great, but it was respectable," Chung says.

This amorphous carbon nitride, although not of diamond's hardness, could protect computer disk drives. Manufacturers had been coating drives with hydrogenated carbon to reduce the wear and tear caused by repeated contact with the reading and recording heads. Chung discovered that amorphous carbon nitride has a wear performance several times better than existing coatings and could be applied by the same sputtering technique that the industry was using to deposit the hydrogenated carbon coatings. By 1997, many manufacturers had adopted amorphous carbon nitride to protect disk drives.

The book on β-C_3N_4 is by no means closed. "We learned how to make carbon nitride way back in 1993 without even knowing it," says Chung.

He and his group had found that titanium nitride, when deposited in a particular crystal orientation, makes a useful foundation for carbon nitride. Following this model, they laid down the materials in several hundred alternating layers, each just 1 or 2 nanometers thick, to form a superlattice.

The hardness of these superlattices turned out to be 45 to 55 GPa—not close to diamond but slightly better than cubic boron nitride, the current second-best material. At first, Chung says he looked at the measurement and said, "Gee, that can't be right." The hardness is intermediate between that of titanium nitride alone and the predicted value for β-C_3N_4, suggesting that they may indeed have the elusive, predicted material.

The numerous false alarms of the past have made them careful not to make a premature announcement, though. "All the evidence we have so far is consistent with the production of β-C_3N_4," says Chung, "but we are not going to make a definitive claim because we are still waiting for additional data to come in." So far, they have "circumstantial evidence," but the proof lies in electron diffraction measurements that should allow the researchers to deduce the exact atomic structure of the layered material.

One of the most valuable outcomes of the search for superhard materials is the ability to design materials and predict their properties, says Chung. "Theoretical tools are now coming of age. Fifteen years ago, it was inconceivable to believe those sorts of predictions. Now, with relative confidence, we can rely on the guidance of these theoretical tools to synthesize materials with specific properties."

The one limitation, Cohen says, is that before calculating the properties, researchers must first choose the elements and the structure out of the myriad combinations possible. "We're good guessers, but we're not great guessers," he adds. The theory still cannot determine which material is the most stable or suggest the best way to make it.

Teter plans to address this issue by developing better computational techniques to design materials from first principles, possibly even finding ways to automate the process.

The failures of the past have given many researchers a more realistic view of synthesizing superhard materials. The search is like "trying to climb the highest mountain, trying to make the most extreme material," says Teter. "In the end, what matters is the performance of a material in its given application." □