EDUARDO CESAR

Versatile Diamonds

Synthetic diamonds are used in dental drills, drilling for offshore oil and as a bactericide

Dinorah Ereno

A new line of 30 dental drill bits with synthetic diamond-coated tips was launched in December 2002 by the company Clorovale Diamonds, in the city of São José dos Campos, São Paulo state. The principal novelty of the drill was the fact that it operates via ultrasound wave vibration, eliminating the unpleasant noise of conventional drills, which rotate at high speeds. Additionally, they promise less painful treatment, eliminating the use of anesthesia in most cases. "Since they are more precise, these diamond drill bits do not cause unnecessary trauma to the teeth," said physicist Vladimir Jesus Trava Airoldi in 2002. Airoldi is a Clorovale partner and pioneer in the development of synthetic CVD (chemical vapor deposition) diamonds in Brazil.

Research with synthetic diamonds—a dark, dull material—began in 1991 when Airoldi resumed his work as a researcher at the National Institute for Space Research (INPE) after completing his post-doctoral studies at the Jet Propulsion Laboratory of the US National Aeronautics and Space Administration (NASA), in Pasadena, California. "My goal was to find a NASA project with a significant scientific aspect, but at the same time very applied," he says.

At the time, synthetic CVD diamond studies were very theoretical—and not as developed as they are today. What

Inside the reactor where diamonds are grown

was known was that synthetics have the same physical and chemical properties as natural diamonds, such as corrosion resistance, large hardness, a low coefficient of friction among solids, higher thermal conductivity and biological compatibility. Because of these properties it is used, for example, as a solid lubricant on satellite solar panel hinges.

Furthermore, with a higher thermal conductivity than all other known materials and a broad optical transmission range, encompassing infrared through X-Rays, synthetic diamonds can be employed in cutting and abrasion tools, protection of surfaces against chemical corrosion, medical and dental tools, optical protectors and other applications. "In the early 1990s, researchers in the United States already envisioned a market worth billions of dollars, as is the case today," he says. "Nowadays, every computer chip has a CVD diamond base because it dissipates heat more quickly."

Initially, Airoldi thought of developing synthetic diamonds for space applications, as heat sinks, solid lubricants and optical protectors. But, given the material's wide range of properties, he wanted to extend its applications to products used in everyday life. The choice of dentistry as a first industrial application of diamonds was the result of a strategy that took into account the fact that dentists appreciate having a technological differential in the office to better serve patients.

Airoldi founded the company Clorovale Diamonds in 1997 to produce synthetic diamond tips for dental drills. Coupled to ultrasound machines instead of traditional rotation devices, they are now sold in domestic and foreign markets. "We are the only company in the world employing the CVD diamond in dentistry," he says.

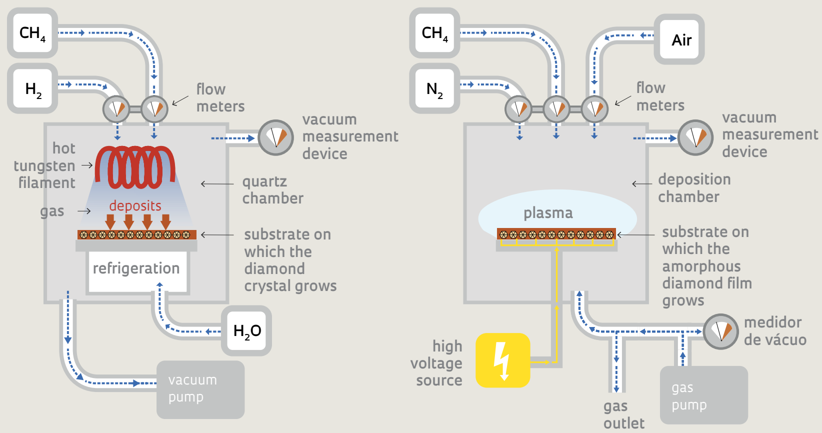
CVD diamonds are produced in small reactors, as a coating in the form of a single stone, using gases such as hydrogen and methane. Traditional drill bits are covered with traditional artificial High Pressure High Temperature (HPHT) diamonds or natural diamonds, but always in powder form welded to a steel rod. The CVD diamond grows on the metal rod itself, covering it in the desired thickness. "These drill bits have minimal wear with use and their service life is greater than that of traditional drill bits," said Airoldi. Furthermore, their manufacture does not use metals or other residues harmful to the environment or to the patient because the raw materials are essentially hydrogen and methane gases.

Clorovale was created with funding from FAPESP through an Innovative Research in Small Businesses Program (Pipe) project. Since then, four other projects have been approved by the Foundation under the same program. Additionally, two thematic projects and three regular research grants have been awarded to Airoldi's group at INPE. The company also received funding in 2006 through an innovation subsidy approved by the Brazilian Innovation Agency (Finep), of the Ministry of Science and Technology.

Today, the researcher has 12 patent filings related to synthetic diamonds. The patent for CVD diamonds has already been granted in the United States, Europe, Australia, Japan and China. "Adherence of the diamond to the metal surface is the most important part of the invention, the object of the patent," says Airoldi. His research group, composed of about 30 people, including researchers, students and postdoctoral grant recipients, has published over 150 scientific articles on diamonds. In recognition of his work, last December Airoldi won the 2011 Finep Innovation Prize in the Innovative Inventor category. On the same occasion, he also

How to make artificial diamonds

The two types, crystalline and amorphous, resulting from the chemical vapor deposition (CVD) process



CRYSTALLINE DIAMONDS

Methane (CH4) and hydrogen (H2) are heated in a chamber. The diamonds grow in small reactors on a metal surface and reach a maximum size of 300 mm.

AMORPHOUS DIAMONDS

Methane, nitrogen (N2) and air mix in giant reactors, allowing manufacture of thousands of pieces each time. Each diamond can measure more than 1000 mm.

received the award for best invention worldwide, granted by the World Intellectual Property Organization (WIPO).

Despite its many attributes, this innovative product took a long time to conquer the market. “We faced many hurdles when we started to sell our product,” says Airoldi. Sales only began to strengthen in 2009, when the company began exporting the product after receiving European Union approval. He believes that the slow response time was due to the fact that consumers resist Brazilian technological innovation. “Even outside of Brazil, our technology is so different that presenting it to potential consumers is not so simple,” he says.

Before being marketed, the new drills were tested by about 500 dentists and the results were very promising. According to Airoldi, dentists who tested the product before its release concluded that treatment was painless in over 70% of cases, because the drill reaches the tooth cavity through vibration, without affecting the dentin, the region where the nerve filaments that lead to tooth sensitivity are located.

In addition to the ultrasound drill bit for dentistry, the company also developed another using conventional rotation with a CVD diamond tip. The technique for coating the two types of bits is similar. The difference is the way the drill bit tip moves, by rotation or vibration. “At the time, obtaining the diamond using the CVD process was very expensive. For this reason, we decided to focus solely on producing drill bits for ultrasound devices, which were a novelty in the market,” says Airoldi.

Almost ten years have passed since Clorovale began marketing its products. During this period, new materials have been incorporated into clinic routines—such as resins and ceramics which require more efficient rotation drill tips—and CVD diamond bits have become more competitive cost-wise compared with traditional bits. Given this new scenario, the company decided to expand its focus and now also produces tips for rotation drills, used mainly in prosthesis laboratories. A CVD diamond drill bit costs about R$200, while the conventional diamond bit is about R$20. “Despite the difference, the cost-benefit ratio is better because the product lasts,” says Airoldi. “They last 20 to 30 times longer than conventional bits.”

Clorovale currently manufactures over 30 models of tips, developed at the request of dentists and professors of dentistry. They are used to remove cavities, resin and amalgam, to wear teeth, for filling finishing and even to cut bone for dental implants—and aided and inspired new courses. “The first ultrasonic dentistry course in Brazil was created at the Bauru campus of the University of São Paulo,” Airoldi said. Today, the campus has two courses, one in the area of dentistry and the other in pediatric dentistry. Other similar courses are taught at the USP School of Dentistry, São Paulo campus, the School of Dentistry at São Paulo State University (Unesp) in the cities of Araraquara and São José dos Campos, both in the state of São Paulo, and more recently at the São Paulo School of Oral Medicine in the city of São Paulo.

In addition to dental drill bits, CVD technology is used in Brazil for deep-sea drilling in search of oil. In this case, small billets of synthetic diamond are embedded in the body of the drill bit through welding or special processes. Initially, the drill was tested for water well drilling. In addition to cutting 30% faster and providing more stability along the drill axis compared to conventional drills with diamond dust tips, the drill was two and a half times more durable. Given these results, Petrobras tested the technology with a prototype specially developed for deep oil wells, with satisfactory results. Further tests are planned for two new prototypes ordered by Petrobras.

Clorovale is focusing on a line of research with what is known as amorphous synthetic diamonds. While crystalline diamonds have an organized carbon atom structure, which results in their extreme hardness, amorphous

PHOTO EDUARDO CESAR **INFOGRAPHIC** TIAGO CIRILLO SOURCE: VLADIMIR AIROLDI/CLOROVALE diamonds do not have a defined structure and are therefore not as sought after. "Still, amorphous diamonds are harder than all known metals," says Airoldi. Amorphous diamonds are also produced using the CVD technique and are called DLC (diamond-like carbon). The basis for manufacturing both types of diamond is basically the same—gases such as hydrogen and methane, halogens like carbon tetrafluoride and other hydrocarbons. They are produced at a temperature above 2300°C in a plasma, which provides the energy needed for nucleation and growth of the diamond coating. Materials such as silicon and quartz and metals such as molybdenum and niobium are also used as substrates during production. But while crystalline diamonds are obtained only in very small regions, measuring a maximum of 200 mm to 300 mm, amorphous diamonds can extend beyond 1000 mm. Another fundamental difference is that crystalline diamonds are made in small reactors, whereas amorphous diamonds grow in immense reactors, allowing production of thousands of items at a time.

Drill tip coated with synthetic diamond for oil exploration

New drills led to the creation of new courses for dentists

Diamond-like carbon, although not as hard as crystalline diamonds, has extremely interesting properties, such as high adhesion to metal surfaces, plus bactericidal and biocompatible characteristics. The bactericidal property is one of the most important, and could be improved if bactericide nanoparticles were incorporated into its structure. "When DLC amorphous diamond is applied to medical instruments or parts of transplants, it also functions as a blood clot inhibitor," says Airoldi. One of the ongoing studies in this area of research is its use for coating the heart valves of artificial hearts. Clorovale has many partners in these studies, including the Federal University of São Paulo (Unifesp) in the city of São José dos Campos, the Vale do Paraíba University (Univap), also in São José dos Campos, and Hospital das Clínicas, of the University of São Paulo. The product is being tested for use in tools used in bone implants in orthopedics and to coat trays used to carry surgical instruments in hospitals.

He also says DLC amorphous diamonds can be used to coat any device or instrument made of stainless steel. When a fine layer of the product is applied, the steel acquires properties such as a low friction coefficient and becomes bactericidal, in addition to being protected against chemical corrosion and mechanical wear. In aerospace, the amorphous diamond will be on the multimission platform of all Brazilian satellites. "We no longer import solid lubrication; everything is made at the INPE laboratory." ■

PROJECTS

1. New materials, studies and innovative applications for CVD diamonds and Diamond-Like Carbon (DLC) - No. 2001/11619-4 (2002-2007)
2. CVD-diamond for a new kind of high-performance tool for drilling and cutting - No. 2006/60821-4 (2007-2010)
3. DLC films for applications in antibacterial, low friction, aerospace, and industrial surfaces and in drill pipes for oil wells - No. 2006/60822-0 (2007-2010)

GRANT MECHANISM
1. Thematic project
2 and 3. Innovative Research in Small Businesses Program (Pipe)

COORDINATORS
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INVESTMENT
1. R$576.456.12
2. R$550,661.41
3. R$505,917.65

SCIENTIFIC ARTICLE

Marciano, F. R. *et al.* Oxygen plasma etching of silver-incorporated diamond-like carbon films. **Thin Solid Films**. v. 517, n. 19, p. 5739–42, 2009.

FROM OUR ARCHIVES

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No fear of the drill
Issue No. 78 – August 2002