Nano-Polycrystalline Diamond Sphere: A Gemologist's Perspective

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Synthetic nano-polycrystalline diamond (NPD) is one of the latest and most exciting results of scientific efforts to synthesize a mineral that has held the fascination of humankind for ages. Unlike other forms of polycrystalline diamond, it is completely transparent. Owing to the material's unique structure, it is also much tougher than natural diamond and previous synthetics, either single-crystal or polycrystalline. This represents a significant breakthrough for industrial purposes and for high-pressure research into the nature and properties of minerals, including diamond.

Naturally occurring polycrystalline diamond (PCD) is highly included. Two types of granular aggregates, referred to as *bort* and *carbonado*, are generally opaque, dark, and unattractive (Orlov, 1973), though some examples have been fashioned into interesting jewelry (Wang et al., 2009). Another form of polycrystalline diamond, of interest for its structure and strength as a model for possible synthesis, consists of the rare naturally occurring fibrous spheres known as *ballas* diamond, found in the Urals, Brazil, and South Africa. Natural aggregates have varying compositions and structural strength, making them inferior to synthesized PCD (Lux et al., 1997).

Gemologists regularly assess diamonds based on certain standard properties. The recently developed NPD sphere invites one to consider those characteristics in a different light and perhaps look with renewed wonder at that which is possible through science and understanding.

The NPD Sphere

A sphere fashioned from diamond: Its very existence seemingly breaks the rules at the heart of our gemological training. How would one cut and polish such a shape out of the world's hardest material, one that also cleaves? Yet this object is actually the fruit of understanding those rules.

The creation of a 7.5 mm NPD orb, described as the world's "first spherical diamond" (Yamada and Yashiro, 2011), was announced in October 2011 by one of Japan's largest newspapers ("Ehime University dazzles…," 2011). This development was quickly followed by a second sphere measuring 5.09 mm (figure 1). Dr. Tetsuo Irifune, the director of Ehime University's Geodynamics Research Center (GRC), kindly offered this author the opportunity to study the latter, a nearly perfect sphere created to study the elastic properties of NPD (Yamada and Yashiro, 2011). In 2003, Dr. Irifune and his colleagues first reported success in producing small NPD pieces measuring approximately 1 mm (Irifune et al., 2003; Sumiya and Irifune, 2008). Today, larger sizes are being manufactured at the GRC as 1 cm (14.5 ct) brownish yellow rods suitable for shaping into forms used in a variety of applications (Irifune and Hemley, 2012).

Figure 1. As this photo demonstrates, NPD is completely transparent. When placed over text on a piece of paper, the 5.09 mm sphere reverses and transmits the letters so that they are clearly legible. Photo by E. A. Skalwold.

The adamantine NPD sphere is deceptively nondescript at first glance, until one considers that it is not a single crystal but a group of nano-sized synthetic diamond crystals packed so tightly that the

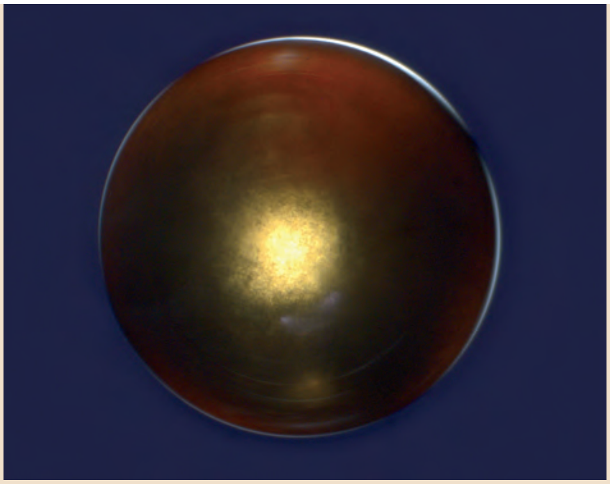

Figure 2. The 5.09 mm NPD sphere displays uniform birefringence between crossed polarizers. Photo by S. D. Jacobsen.

material is tougher than either PCD or single-crystal diamond (SCD)—and essentially flawless and completely transparent (again, see figure 1). This transparency stems in part from a manufacturing process that creates atomic bonding between individual nano-size crystals, interlocking them and thus minimizing the scattering of light waves along grain boundaries, while also minimizing voids and impurities that might contribute to scattering (T. Irifune, pers. comm., 2012). Earlier synthetic PCDs required the addition of metals such as cobalt, which produced a less transparent and weaker material (Irifune et al., 2003). But NPD contains only trace impurities: 100–200 ppm hydrogen, 10–30 ppm oxygen, 50–100 ppm nitrogen as aggregates (dispersed nitrogen <0.5 ppm), and <1 ppm boron (Sumiya et al., 2009).

Although diamond is optically isotropic, natural diamond often displays a birefringence pattern caused by lattice strain. In NPD, the crystals' random orientation results in a similarly isotropic solid, but with a uniform birefringence. Observation of the sphere between crossed polarizers revealed this very condition (figure 2). This is quite different from SCD, where birefringence often exposes a specimen's synthetic origin—or, in the case of natural diamond, reveals underlying strain associated with inclusions or structural weakness or even evidence of treatment. In fact, laboratory analysis detected no large lattice strain in NPD (Sumiya et al., 2009). The sphere's brownish yellow color has been attributed to lattice defects in each synthetic nano-diamond crystallite, which are analogous to those found in brown type IIa diamond and result from plastic deformation brought on by high-pressure, high-temperature (HPHT) growth (Sumiya et al., 2009). It is unknown what causes NPD's reddish orange fluorescence observed under long-wave UV radiation (a slightly weaker reaction is seen under short-wave UV).

What is the significance of the prefix "nano"? Consider that the diameter of a human hair is somewhere between 50,000 and 100,000 nm. NPD is actually a mixture of two forms of synthetic diamond: 10–20 nm equigranular crystallites and 30–100 nm lamellar crystalline structures (Sumiya and Irifune, 2005). Both are formed during a sintering process used to convert pure graphite directly into cubic synthetic diamond in a matter of minutes (Irifune et al., 2003). How is this possible? The GRC utilizes a 6,000-tonne multi-anvil apparatus (figure 3) to achieve the required pressure of 15 gigapascals (2.18 million psi) and temperature of 2,300–2,500°C (Irifune et al., 2003; Irifune and Hemley, 2012). Interestingly, lower temperatures in the 1,600–

Figure 3. The GRC's large-volume, multi-anvil press uses a 6,000-tonne hydraulic ram to synthesize NPD rods up to 1 cm long. The two young GRC staff members are wearing traditional costumes from a famous Japanese novel set in Matsuyama, the city where the facility is located. Photo courtesy of T. Irifune.

Figure 4. Using pulsed lasers, it is possible to fashion nearly any shape from NPD, including the 7.5 and 6.0 mm round brilliants shown here. The NPD rods range from 6.5 to 8.0 mm in diameter. Photo courtesy of T. Irifune.

2,200°C range produced some areas of hexagonal synthetic diamond—or *lonsdaleite*, an allotrope of diamond associated with meteoritic impact, which is a naturally occurring HPHT event (Irifune et al., 2003; Sumiya and Irifune, 2005; Ohfuji and Kuroki, 2009). The lamellar structures observed in NPD apparently originate in a lonsdaleite phase produced during the sintering process. This phase and the euhedral granular structures present in NPD are directly related to the crystallinity of the graphite starting material (Ohfuji and Kuroki, 2009).

While diamond is considered the hardest material in nature, diamond crystals do not have the same hardness in all crystallographic directions. In addition to its transparency, NPD is tougher than natural diamond, and it is uniformly as hard as the hardest direction of any single-crystal diamond. The NPD grown by the GRC group also has better hardness than other forms of synthetic polycrystalline diamond and displays superior mechanical properties at high temperature (Sumiya and Irifune, 2007a, b). How? As explained above, within NPD the crystallites are solidly bonded to each other, essentially interlocking. This reduces or nearly eliminates breakage along grain boundaries (Sumiya and Harano, 2012), while the lamellar structure adds toughness against fracturing within the grains (Sumiya and Irifune, 2008). Because the crystals are randomly oriented, there is no particular cleavage direction in NPD, whereas SCD cleaves along planes parallel to its octahedral faces and less easily along its dodecahedral faces (Field, 1992). This weakness becomes problematic during high-pressure research, and also puts at risk diamonds set in rings exposed to sharp blows. That makes NPD an interesting possibility for jewelry subjected to heavy wear.

The unique nature of NPD allows it to be fashioned into a virtually unlimited variety of shapes with uniform properties in all directions, including spheres and round brilliant gems (e.g., figure 4). But NPD's hardness and toughness pose a daunting problem when it comes to cutting and polishing, a necessity for many kinds of applications such as the diamond anvil cell. This instrument uses two diamonds oriented culet to culet, not only for applying pressure but also as windows for viewing a sample under study.

While an SCD specimen can be cut with lasers, the polishing is accomplished with diamond abrasives. Not so for NPD, whose polycrystalline nature dictates that the hardest direction of many of its crystallites will always be exposed to the surface, making abrasives far less effective. Pulsed lasers are the only method for successfully cutting and fine finishing NPD. These lasers work by converting diamond to graphite, which can then be removed by several means. Researchers found that micromachining with a nano-pulsed near-ultraviolet laser produces a smooth undamaged surface on NPD, but generates micro-cracks and micro-cleavages during processing of single-crystal diamond (Odake et al., 2009). A later study by Okuchi et al. (2009) concluded that the most efficient method involves three types of pulsed lasers used in combination: near-infrared for rough shaping, and ultraviolet and femtosecond lasers for fine finishing.

Future Possibilities

The development of high-quality nano-polycrystalline synthetic diamond has been made even more fascinating by the opportunity to observe a sphere of the material firsthand. With its superior hardness and toughness, NPD can be fashioned into a virtually endless array of shapes using lasers. Its implications for the gem industry presently lie within research applications. Nevertheless, improvements in color and production efficiency may soon make NPD a beautiful and sought-after synthetic gem material.

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