CLUES TO THE PROCESS USED BY GENERAL ELECTRIC TO ENHANCE THE GE POL DIAMONDS

By Karl Schmetzer

The specific details of the process used to enhance color and clarity in GE POL diamonds have not been disclosed. However, a survey of U.S. patents and European patent applications reveals that General Electric has developed a variety of high-temperature annealing techniques at different pressures for enhancing the optical properties of polycrystalline synthetic diamond films and single-crystal synthetic diamond. These methods may provide important clues to the process being used to decolorize natural type IIa (GE POL) diamonds, that is, by reducing the structural defects associated with their brown coloration.

In March 1999, a new type of enhanced diamond was announced by Pegasus Overseas Limited (POL) of Antwerp, Belgium, a subsidiary of Lazare Kaplan International (LKI) Inc. (*Rapaport NewsFlash,* March 19, 1999; see figure 1). This new method, which was developed by the General Electric Company (GE), reportedly changes both the color and clarity appearance of certain diamonds (see Tempelsman, 1999). The faceted diamonds are referred to as GE POL, Pegasus, and most recently at retail, Monarch™ diamonds (Heeger, 1999). Almost immediately after the GE process was announced, numerous questions were raised about the identification of these enhanced natural diamonds (see, e.g., *Rapaport NewsFlash,* 1999; Even-Zohar, 1999).

Although GE has confirmed that it is using a high-pressure, high-temperature (HPHT) process, details of the treatment conditions so far have not been disclosed (see, e.g., Johnson et al., 1999; Moses et al., 1999; Shigley et al., 1999). Consequently, the exact enhancement mechanism still is unknown. However, a statement made by Bill Woodburn, General Electric's vice president of Superabrasives, provides some insight into GE's approach (Woodburn, 1999): "In nature the diamond's color is disturbed by normal geological factors such as changes in heat and pressure or contamination that disturbs the conditions that allow the stones to reach their colorless potential. The GE process,

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Figure 1. These three GE POL diamonds (4.11–5.34 ct) were all decolorized by a high-pressure, high-temperature process developed by General Electric. Photo by Elizabeth Schrader.

through high temperature and pressure, attempts to recreate the earth's geological process and allows the diamond to reach its optimal colorless potential." That is, GE proposes that its process simulates the conditions of heat and pressure to which the diamond might have been exposed naturally in the earth's mantle.

Given this situation, the present author conducted a search of diamond treatment patents to find any reference to a process that might provide better understanding of the method applied. It is hoped that better knowledge of the enhancement mechanism will help in the development of identification criteria.

BACKGROUND

Primarily on the basis of their nitrogen or boron contents, diamonds are classified as types I (a and b) and II (a and b). The vast majority of natural diamonds are type I, which contain different forms of nitrogen. Type IIa diamonds lack nitrogen and boron (as detectable by standard infrared spectroscopy), whereas type IIb diamonds typically contain boron (for more on diamond types, see Fritsch and Scarratt, 1992; Weldon, 1999). In a sample of more than 800 GE POL diamonds examined by the GIA Gem Trade Laboratory, 99% of the stones were determined to be type IIa (i.e., low-nitrogen) natural diamonds (Moses et al., 1999). Because type IIa diamonds do not absorb visible light unless they contain structural defects, they are usually colorless; if such defects are present, however, type IIa diamonds may be gray, brown, or even pink (Fritsch, 1998; Lu et al., 1998). LKI president Leon Tempelsman has stated that the starting material for the GE process consists primarily of "top brown" to brown diamonds (see Donahue, 1999; compare Even-Zohar, 1999; Levy, 1999). Thus, the color alteration in natural brown type IIa diamonds could be caused by healing the structural defects within the diamond by means of plastic flow (also called plastic deformation).

Color improvement by high-pressure, high-temperature annealing processes was independently developed and patented in the late 1970s by GE (Strong et al., 1978, 1979) and the De Beers Industrial Diamond Division (Evans and Allen, 1983). Both procedures were based on the transformation of type Ib nitrogen to type Ia nitrogen, thereby reducing the saturation of a yellow or brownish yellow color in diamonds (Schmetzer, 1999). Although this mechanism may be involved in a few of the Pegasus diamonds examined so far, it cannot be the main mechanism for color and clarity improvement of these type IIa diamonds because they lack significant amounts of nitrogen.

GE has announced that it has not patented the process to "whiten" the diamonds sold by POL (Barnard, 1999; Donahue, 1999; Weldon, 1999). The reasons for this may be that: (1) GE wishes to keep details of the process proprietary, (2) the process is already patented, or (3) the process is already considered public domain and thus can no longer be patented. The following review of related patents suggests that all of these reasons may apply to some extent.

RELATED PATENTS

The synthetic diamond treatments described in a series of patent applications filed originally in 1994 by General Electric may help shed some light on the present treatment process of Pegasus diamonds. All involved enhancing the "toughness" of, and "reducing crystalline defects" in, chemical vapor deposited (CVD) synthetic diamond. (In the following, the terminology used in these patent documents has been adopted as closely as possible, so some of the wording may seem a little awkward.) The original patent application was filed March 11, 1994, in the U.S., but was later abandoned and so never resulted in a U.S. patent. This same application was refused by the European Patent Office in 1998 in the course of the European examination process, but by 1995 it had already entered the public domain (Anthony et al., 1995a).

Subsequent to the March 1994 application, four related patent applications were filed by GE in May and June of 1994. Three of these received U.S. patents (No. 5,672,395; No. 5,451,430; and No. 5,468,934). The methods described in these patents reveal improvements that bring us even closer to understanding the high-pressure, high-temperature technique being used to enhance color and clarity in the Pegasus diamonds.

The Original March 1994 Patent Application. As described in the European application that was subsequently abandoned (Anthony et al., 1995a), this HPHT treatment of CVD synthetic diamond can be applied to single crystals or polycrystalline diamond material up to 10 mm thick that contains grain boundaries, growth defects, dislocations, plastic strain, or other sources of density fluctuation (concentrations of inhomogeneities or voids) that reduce the quality of the optical properties.

In the process described, the synthetic CVD diamond is brought into the high-pressure, high-temperature conditions under which diamond is the thermodynamically stable phase of carbon for a prescribed period of time. The starting material is placed in inert pressure-transmitting fluids or solids, including salts (e.g., sodium chloride or potassium chloride), oxides, or graphite, and subjected to (preferably) pressures of 50–70 kilobars and temperatures of 1400°C–1700°C. In this region of the diamond stability field (see figure 2), both plastic flow (deformation) and atomic diffusion of carbon occur. The synthetic diamond may be held under these conditions for a period that ranges from minutes to several days, but typically is from 1 to 24 hours. Subsequent to cooling and release of pressure, the result is a diamond with fewer defects, reduced density gradients, and lower stress—that is, with improved optical properties. If color centers related to defects are responsible for a brown coloration, and such defects are present, one can also assume that the removal of such defects will "remove" or lighten the original color.

This HPHT method appears to use pressures and temperatures that are similar to those used in the earlier technique developed and patented by GE at the end of the 1970s for transformation of type Ib to type Ia nitrogen in natural and synthetic diamonds (again, see Strong et al., 1978, 1979). The new GE POL method, however, must use a completely different mechanism for color and clarity enhancement, because of the absence of nitrogen in the type IIa diamonds treated.

The Subsequent GE Patents. Whereas the procedure described in the 1994 patent application involved treatment in the diamond stability field (very high pressure), the later GE patents describe diamond treatments under conditions within the graphite stability field (lower pressure), but with almost identical results.

In U.S. patent 5,672,395, Anthony et al. (1997) describe an HPHT treatment (again, with specific reference to CVD synthetic diamond) that uses plastic deformation to improve diamond properties by reducing strain and decreasing the size of voids. Typical pressures of 5 kilobars were applied at temperatures between 1600°C and 1900°C. These conditions are above the plastic yield limit line but below the diamond-graphite boundary; that is, they are within the graphite stability field (again, see figure 2). To prevent graphitization of diamond while plastic flow is occurring during the high-temperature annealing, hydrogen gas or a mixture of hydrogen and methane plus other nonoxidizing media can be used as graphitization suppressors. Also to prevent graphitization, the annealing time at 1800°C is kept below 60 minutes, and at 1900°C it is below 15 minutes. This method is less expensive than that mentioned above simply because a lower-pressure apparatus can be used.

In U.S. patent 5,451,430, Anthony et al. (1995b) used temperatures between 1600°C and 1900°C, but at even lower pressures, to improve the toughness of CVD synthetic diamond. Graphitization suppressors again were used (e.g., hydrogen gas or a mixture

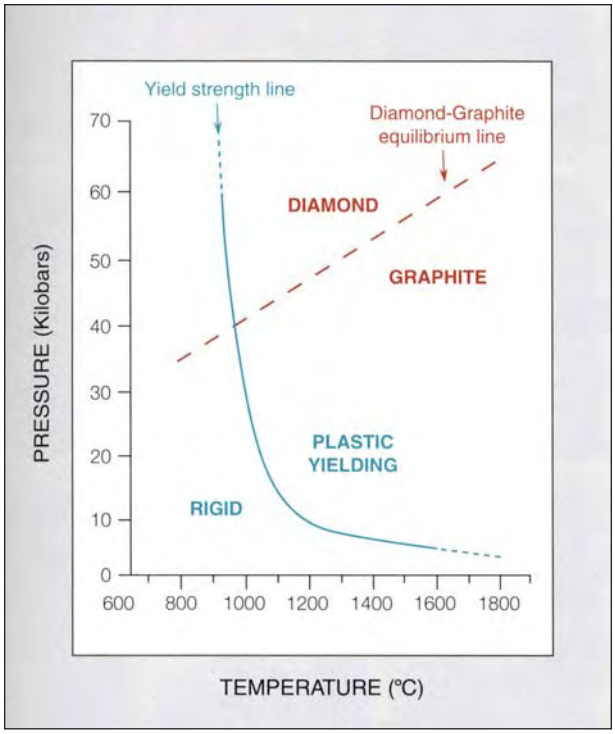

Figure 2. This pressure-temperature diagram illustrates the diamond-graphite stability field (defined by the dashed equilibrium line) and the plastic yield limit of diamond (solid line). Diamond is the stable form of carbon above the diamond-graphite equilibrium line, whereas graphite is stable below this line. Diamond is rigid to the left of the yield-strength line, whereas it can plastically deform under conditions corresponding to those to the right of this line. Modified from DeVries (1975); see also Anthony et al. (1995a and b, 1997).

of hydrogen and methane—or, alternatively, inert atmospheres such as argon, helium, or neon), and pressures could vary between 1 torr and 5 atmospheres (i.e., significantly less than one kilobar). Under these conditions, the annealing time is further reduced, to prevent graphitization, to less than 6 minutes at 1800°C and less than 15 seconds at 1900°C. Again, plastic deformation that occurs at high temperatures eliminates stress in the synthetic diamond (single crystals or polycrystalline material) and improves the optical properties. In U.S. patent 5,468,934, Anthony and Fleischer (1995) describe an apparatus designed to perform the technique discussed in this paragraph.

CONCLUSION

Information as to the exact pressures, temperatures, and annealing times applied by General Electric to produce the Pegasus diamonds, as well as which pressure-transmitting media and/or graphitization suppressors actually are used, is still proprietary. However, at least part of the mechanism of color (and clarity) enhancement may be better understood by the information cited in the GE patent applications and patents discussed above, which are probably precursors of the current GE POL process.

The different high-temperature annealing techniques at variable pressures described in these documents for polycrystalline synthetic diamond films and single-crystal synthetic diamond also can be applied to natural diamonds. It also should be possible to reduce the structural defects associated with the brown coloration of some natural diamonds (again, see Fritsch, 1998; Lu et al., 1998) by carefully controlled plastic deformation at temperatures above 1600°C. The observation of strain patterns and of graphite in cleavages in Pegasus diamonds (Shigley et al., 1999; Moses et al., 1999) also may be explained by plastic deformation during treatment and by graphitization along cleavages. However, it must be kept in mind that new methods and new discoveries are always possible, and GE still has not revealed the details of the actual conditions being used for its Pegasus diamonds.

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