

# Direct Conversion Sintering of Super-hard Nano-polycrystalline Diamond from Graphite

Hitoshi Sumiya<sup>1,a</sup>, Tetsuo Irifune<sup>2,b</sup>

<sup>1</sup>Electronics & Materials R&D Laboratories, Sumitomo Electric Industries, Itami 664-0016, Japan

<sup>2</sup>Geodynamics Research Center, Ehime University, Matsuyama 790-8577, Japan

<sup>a</sup>sumiya@sei.co.jp, <sup>b</sup>irifune@dpc.ehime-u.ac.jp

## Abstract

*High-purity and super-hard nano-polycrystalline diamond has been successfully synthesized by direct conversion from high-purity graphite under static pressures above 15 GPa and temperatures above 2300 °C. This paper describes research findings on the formation mechanism of nano-structure and on the contributing factor leading to high hardness.*

**Keywords :** Synthetic diamond, nano-polycrystalline diamond, high pressure, direct conversion

## 1. Introduction

Recently we have succeeded in the reproducible synthesis of a homogeneous high-purity polycrystalline diamond by direct conversion from graphite under static ultra-high pressure and high temperature [1]. This polycrystalline diamond has been turned out to have remarkable characteristics in terms of microstructure and mechanical properties as we reported previously [2, 3]. The high-purity nano-polycrystalline diamond has an immeasurable potential for industrial uses such as cutting tools and abrasion-resistance materials, because of its extremely high hardness, no cleavage feature and high thermal stability.

Here, we report the experimental results for synthesis and characterization of the polycrystalline diamond from graphite, and show some new research findings on the formation mechanism of such nano-structure and on the contributing factor leading to such high hardness. These findings were derived from comparative experiments using various carbon materials as the starting material.

## 2. Experimental

Polycrystalline diamond specimens were synthesized from high purity well-crystallized polycrystalline graphite by the direct conversion method under high-pressure and high temperature. The graphite was enclosed in a Re capsule, and high-pressure and high-temperature (HPHT) conditions (12-21 GPa, 1500-2700 °C, 10-10000 sec) were generated with a Kawai-type multi-anvil using a separate electrical heater of Re or LaCrO<sub>3</sub>. For comparison, non-graphitic carbons such as carbon black (CB), grassy carbon (GC), C<sub>60</sub> and CNT were used as the starting material. The recovered sample was examined using an

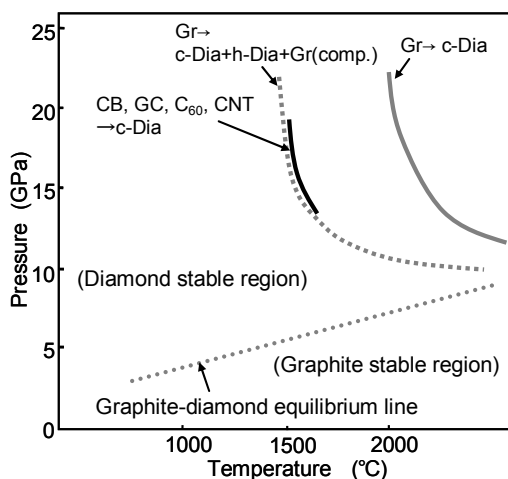
x-ray diffractometer. The microstructure of polycrystalline diamond was investigated by transmission electron microscopy (TEM). The hardness of the specimen was evaluated by an indentation test using super-hard diamond Knoop indenters prepared from synthetic type IIa diamond crystals [4].

## 3. Results and Discussions

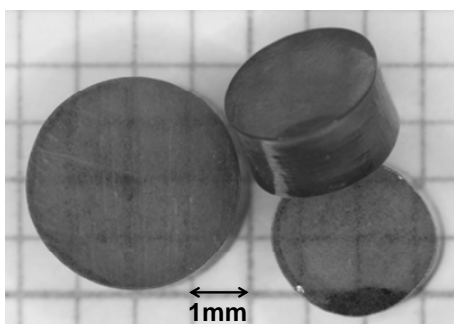
Figure 1 shows the experimental results of the direct conversion from graphite to diamond under various high-pressure and high-temperature conditions. Near the broken line in the figure, graphite begins to convert to cubic diamond (c-Dia) and hexagonal diamond (h-Dia). The unconverted graphite remains as compressed graphite (comp. Gr). Above the solid line, graphite converts to cubic diamond completely, and well-sintered and high-purity polycrystalline diamonds can be obtained. The specimen exhibits transparency, as shown in Fig. 2, indicating very few heterogeneous phases and impurities. The onset temperatures for diamond formation from non-graphitic carbon materials (CB, GC, C<sub>60</sub>, CNT) were found to be unexceptionally 1500-1600°C (at 15-21 GPa), which correspond to the onset temperature from graphite shown as the broken line in Fig. 1. The formation of hexagonal 2H diamond and the marked graphitization were negligible from non-graphitic carbons. Above the onset temperature, the non-graphitic carbon phases convert to cubic diamond completely, whereas graphite transforms to cubic diamond partially.

The high-purity polycrystalline diamond obtained from the well-crystallized graphite has a fine mixed texture of a homogeneous structure consisting of randomly oriented nano-diamond particles (10-30 nm) formed in a diffusion

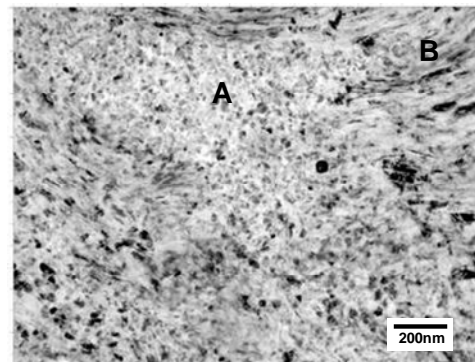
process and a lamellar structure consisting of (111) layered diamonds formed in a two-step martensitic process via the hexagonal diamond phase (Fig. 3 [2]). Each graphite particle of the starting material is deformed differently under high pressure because the direction of the maximum compression force on graphite lattice differs from one particle to another. The differences in the direction of maximum compression force on graphite particles seem to create different conversion paths (diffusion and martensitic processes) to cubic diamond, leading to the mixed texture. On the contrary, all of the polycrystalline diamonds synthesized from non-graphitic carbons (CB, GC, C<sub>60</sub>, CNT) consist only of a fine homogeneous structure without a lamellar structure and containing no hexagonal diamond phase. This fact indicates that the nano-polycrystalline diamonds from non-graphitic carbons have formed only in a diffusion process. Nano-polycrystalline diamonds consisting only of single-nano particles (less than 10 nm) can be obtained from non-graphitic carbons at 1600-2000 °C under pressures more than 15GPa.



**Fig. 1 Results of high pressure and high temperature experiments of direct conversion from graphite and non-graphitic carbon to diamond.**



**Fig. 2 High-purity polycrystalline diamond synthesized directly from graphite.**



**Fig. 3 TEM images of high-purity polycrystalline diamond synthesized directly from graphite at 18 GPa, 2500 °C, 10sec. A: homogeneous fine structure, B: Lamellar structure.**

The Knoop indentation hardness of polycrystalline diamond from graphite is as high as 120-145 GPa, which is equivalent to that in (001)<100> of synthetic type IIa diamond crystal and obviously higher than those of the common type I natural or synthetic diamond crystals. The distinctive feature of the microstructure (very fine, dense, no secondary phases) seemed to lead to the extremely high hardness. However, the hardness values of nano-polycrystalline diamonds consisting only of single-nano particles (70-90GPa) are significantly lower than that of polycrystalline diamond from graphite. It is assumed that the excessively small size of diamond particles dominate the inter-granular sliding. (reverse Hall-Petch effect). And it is also possible that the absence of the lamella structure reduces the dislocation blocking effect.

#### Acknowledgements

The authors thank Dr. Yusa of NIMS (Tsukuba, Japan), for his kind help on this work.

#### References

- [1] T. Irifune, A. Kurio, S. Sakamoto, T. Inoue, H. Sumiya, *Nature*, 421, 599 (2003).
- [2] H. Sumiya, T. Irifune, A. Kurio, S. Sakamoto, T. Inoue, *J. Mater. Sci.*, 39, 445 (2004).
- [3] H. Sumiya, T. Irifune, *Diamond Relat. Mater.*, 13, 1771 (2004).
- [4] H. Sumiya, *Rev. Sci. Instrum.*, 76, 026112 (2005).