

## Decomposition of chlorinated organic compounds to diamond structured carbon at moderate hydrothermal conditions

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In spite of unique physical and chemical properties a diamond is used only to selected application due to high costs and limited sizes the both synthetic and natural single crystals. Hydrothermal processes are very attractive to overcome the limitations of usual diamond synthesis methods for the purpose to grow diamond in like manner with quartz and emerald. However there are a few publications on the hydrothermal diamond synthesis. Hydrothermal reactions have been fulfilled in piston-cylinder device, using liquid reagents 1,1,1-Trichloroethane, 10M NaOH and hydrogenated diamond seeds. Copper container with reagents was loaded up to 1GPa and slowly heated to 300°C. The experiment duration was 1-3 days. After two-step acid treatment (guaranteeing a presence only diamond structured carbon) the several samples complete differed in size, shape, and structure from used seeds have been elicited in hydrothermal reaction products. These samples exhibited high stability in air oxidation conditions and displayed (111) and/or (200) diamond peaks on micro-XRD pattern.

Key words: amorphous carbon, diamond film, diamond-like carbon

### 1. INTRODUCTION

At present diamond is effectively produced by melt (HPHT) [1], gas (CVD) [2] and shock-wave [3]. However, the question about of natural diamond genesis is still debated and the accumulation knowledge in alternative methods of diamond growth is continued. Recently some attempts to overcome the limitations of usual synthesis methods through radically different processes, for example, rapid nonhydrostatic compression of C<sub>60</sub> at room temperature [4], extracting silicon from silicon carbide in chlorine-containing gases at ambient pressure [5], selective leaching of silicon carbide by high-pressure, high-temperature water [6] have been done. A review of liquid phase systems pertinent to diamond synthesis was adduced [7] and hydrothermal synthesis of diamond by low-pressure liquid phase epitaxy on seeds was presented [8,9]. Hydrothermal growth of diamond in metal-C-H<sub>2</sub>O system was achieved [10]. However, as fairly noted [11] for both [8,10] the problem is proving that there is new growth of diamond in the presence of diamond seeds. Here we report that diamond structured carbon have been synthesized through namely hydrothermal reaction of liquid according to P-T conditions [12] reagents: 1,1,1-Trichloroethane and 10M NaOH solution in the presence of hydrogenated natural diamond seeds at 300°C and 1GPa pressure without any catalyst metals.

### 2. EXPERIMENTAL DETAILS

Hydrothermal reaction has been fulfilled in piston-cylinder device [13]. Two types of copper container 0.6 ml and 7 ml volume were used in our experiments. Natural diamond powder 5000 and 325# (Osaka Diamond Industrial Co., Ltd) have been firstly hydrogenated similarly to [14].

Our approach was to conduct hydrothermal reaction at the certain artificially created surfaces. So, several pellets containing 2g/cm<sup>3</sup> of 5000# or 4 g/cm<sup>3</sup> of 325# diamond seeds have been prepared after mixing with Cu powder (Wako Pure Chemical Industries, Ltd.) by pressing in steel mold at 150MPa load. In contrast with free seeds in the case of fixed ones the new growth can easily pass only on the surface of pellets preferably as film.

Hydrogenated (h-diamond) powder and/or Cu-combined seeds were placed on the bottom of copper container with liquids reagents 1,1,1-Trichloroethane (C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub>) and 10M NaOH both (Wako Pure Chemical Industries, Ltd.) in proportion 1:2. Then sealed copper container was loaded up to 1GPa in piston-cylinder type high-pressure vessel and slowly heated up to 300°C with different heating rate (0.1-1.2 °/min). After 1-3 days exposure the reaction products have been extracted, ultrasonic cleaned in distilled water and acetone. Then two steps of acid treatment were applied. Firstly ballast products NaCl, CuCl<sub>2</sub>·Cu(OH)<sub>2</sub>, NaCuO were eliminated after treatment in Aqua regia during 24h at room temperature.

### 3. RESULTS AND DISCUSSION

Hydrothermal conditions are far from equilibrium for diamond growth, therefore some non-diamond carbon can appear. For example, in the experiments without diamond seeds we found only amorphous carbon, no graphite or other carbon forms regardless of different organic precursors. For effective removing of amorphous carbon we used two approaches. One is boiling in mixture of sulfuric acid and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> during 2-4h. Another is elimination of surface non-diamond carbon by oxidation in air.

After two steps of acid treatment (experiment with free seeds) the reaction products had white color and did not reveal any differences in X-Ray diffraction (XRD) and Raman shift data in comparison with initial diamond seeds. However, during air oxidation test (Thermoplus TG 8120) some features become discernible. The data of differential thermal analysis (DTA) are shown in Fig. 1. So, hydrogenation of initial diamond causes shift of oxidation reaction rate maximum (708°C DTA effect) to higher temperature region in comparison with initial seeds. Increasing of oxidation resistance occurs due to removing of surface defects during hydrogenation at high temperature. The products after hydrothermal synthesis are characterized by small amount of amorphous carbon, which completely burned out until 600°C, peak at 727°C corresponding to 5000# h-diamond seeds. However, peak at 858°C is important because it means that some coarse diamond grains appeared.

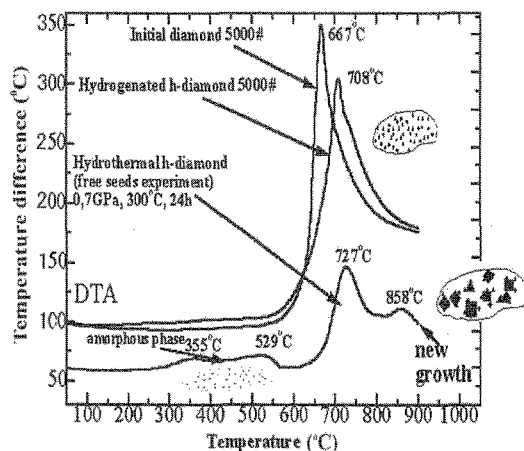


Fig. 1 DTA curves of non-isothermal oxidation in air with heating rate 10°/min. Hydrothermal h-diamond was firstly subjected two steps acid treatment.

Thus, DTA data are very effective for separation of different carbon materials. Moreover, during modeling tests we have found that DTA data are also sufficiently sensitive to grains size of diamond subjected to air oxidation. So, we have been able easy make the apparent coarse diamond grains mixed with fine as base component.

The suggestion about of coarsening initial seeds through hydrothermal reaction was confirmed after careful optic and electron microscopy studies of samples treated with two steps of acid processing. So, Fig. 2 (c-d) demonstrates the scanning electron microscopy (SEM) images (HITACHI S-4700T) of diamond polycrystals shaped as globules and initial seeds (a, b) at approximately same magnification. It is obviously that globules were produced through sintering of initial 5000# seeds (Fig. 3 (a)) and according to energy dispersive X-Ray microanalysis (EDX) have no impurities besides carbon and oxygen similar to initial h-diamond seeds (Fig. 3 (b)).

More interesting results were obtained after experiments with fixed seeds. So, the transparent plates

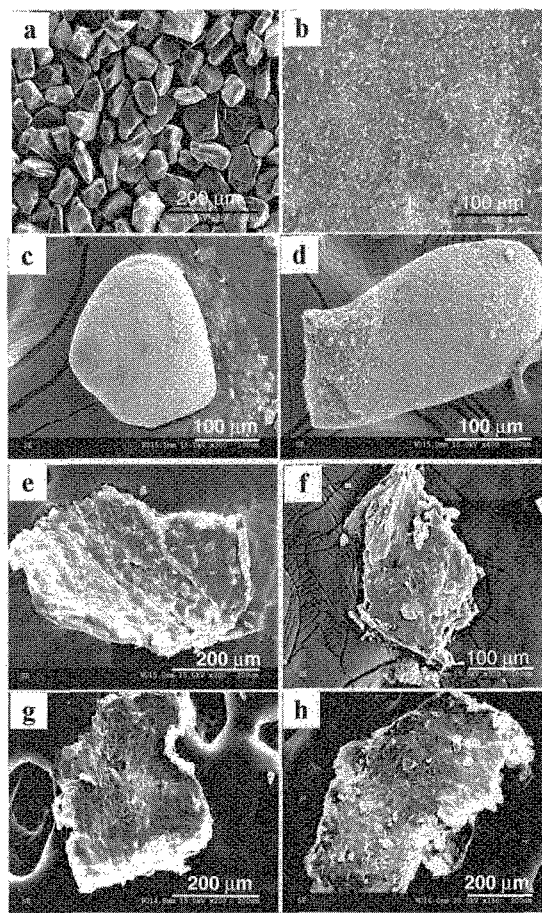


Fig. 2 SEM images showing size and shape of hydrothermal synthesis products after two steps acid treatment: c-h and initial seeds: a -325# and b - 5000#.

considerably differed in size, shape and surface morphology from used seeds have been elicited in acid treated reaction products (Fig. 2 (e-h)). These 200-500 μm size plates (average size of 5000# and 325# seeds composes 1 and 45 μm respectively) are certainly new growth, characterized by raised oxygen concentration in comparison with seeds and sintered globules (Fig. 3(c)). Furthermore, ones have exhibited high stability similar to coarse 325# natural diamond seeds in air oxidation condition at heating up to 1000°C with heating rate 10°/min. Figure 3 (d) demonstrates the surface structure of large hydrothermal carbon plate after air oxidation with appropriate EDX data.

Sufficiently large size of carbon plates has permitted us to separately expose to micro X-ray diffraction (μ-XRD) of everyone. So, according to μ-XRD data (JEOL JDX-3530, 30μm collimator) and (M21X MAC Science Co., Ltd, 100μm collimator) these plates have contained amorphous (Fig. 4) or rather nanocrystalline diamond phase, because the diamond growth outside its thermodynamic stability is preferably continued as nanocrystalline diamond-structured carbon with average size nanocrystals of 5-10 nm [5]. However, some plates

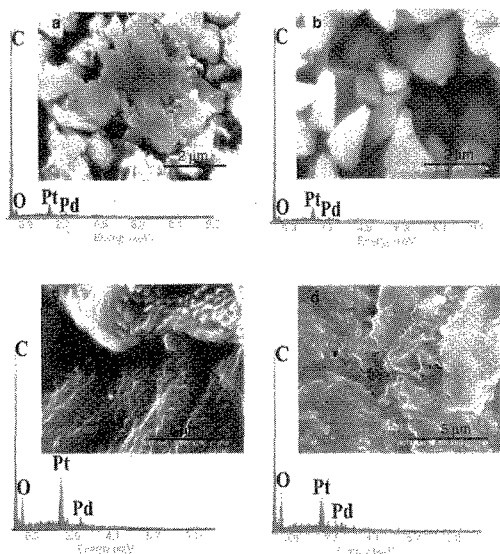


Fig. 3 Surface structure of hydrothermal products **a,c,d** and initial 5000# seeds **b** with appropriate EDX data; **a** – produced by sintering of independent seeds and **c,d** – grown on the surface of Cu-diamond pellets; **a,c** – after two steps acid treatment and **d** – after 24h exposure in Aqua regia and heating up to 1000°C in air.

were displayed (111) and (220) diamond peaks (Fig.4 (b, c)) even after heating up to 1000°C in air (Fig.4 (c)). Of course, during growth the new phase can involve in some amount of seeds from the surface of copper templates. However, we did not find any presence of initial seeds on the surface of large plates, which were analyzed by  $\mu$ -XRD. Moreover, the number of diamond grains in Cu-pellets surface layer were very few and cannot be estimated XRD. In addition, starting diamond powder 5000# are completely disappeared after heating up to 1000°C in air while hydrothermal produced diamond structured plates are remaining in unburned rest (Fig.3(d)).

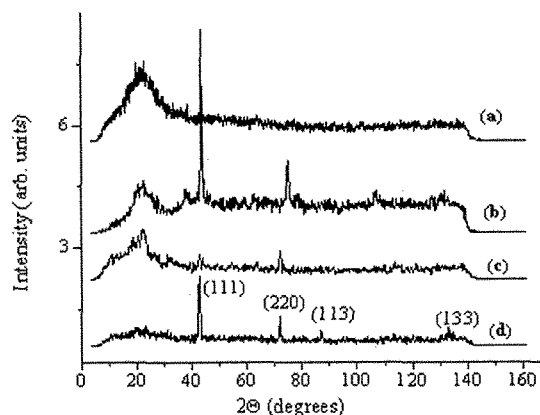
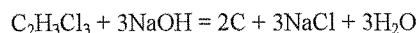


Fig. 4 Micro XRD patterns of hydrothermal carbon plates **a-c** and initial 5000# seeds **d**; **a,b** – after two steps acid treatment and **c** – after 24h exposure in Aqua regia and air oxidation at 1000°C.

At this stage we do not know a mechanism for hydrothermal growth process. Perhaps, the mechanism

of new diamond growth is condensation-polymerization. Firstly 1,1,1-Trichloroethane easily decomposed under alkaline hydrothermal conditions [15] as a result the colloidal solution containing unstable and very active carbon can be produced according to following equation:



Then diamond growth may occur by insertion of active C species into C-H bonds of hydrogen terminated diamond surface. For example, according to [16] the energy barriers for addition of  $\text{C}_2$  to diamond surface are small during diamond thin film growth from fullerene precursors.

It should be noted that we did not use any catalyst metals (usual Ni-Fe-Mn or Co). Pure copper is not catalyst for diamond synthesis [17] and produced diamond is certainly free of metallic elements (according to EDX data) similar to natural diamond [11].

#### 4. CONCLUSIONS

There are only a few publications on the real hydrothermal diamond synthesis. At present, only Szymanski, et al. has produced the low-pressure liquid phase epitaxy of diamond seeds and the results of [6], [10] are rather related to CVD process, because the temperature in both methods was 800°C and pressure 100 and 140 MPa respectively.

This study coordinates with results of Szymanski's group and confirms that hydrothermal diamond growth is possible and should be involved in the origination of natural diamond.

As diamond-structured carbon has been synthesized using liquid organic precursor in soft hydrothermal conditions then the growth of diamond in Nature can be continued in colloidal pneumatolytic-hydrothermal environment during travelling of cubic diamond formed in kimberlitic magma on the depth 100-250 km to the near surface layers 1-10 km depth.

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