

# Experimental study of the structure of milled diamond-containing particles obtained by the detonation method

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**Abstract.** A diamond-containing material (DCM) produced by detonation was mechanically milled using KM-1 and AGO-2S mills. Experimental spectra for infrared (IR) absorption, Raman scattering and X-ray diffraction patterns (XRD) were obtained for the treated DCM samples. We compared the Raman and IR spectra for the KM-1 milled samples and concluded that the surface of the DCM particles was not uniform. The mechanical force that resulted from milling with the AGO-2S destroyed the non-diamond part of the particles and initiated irreversible physical and chemical changes in them. The destruction of the diamond grains was the consequence of these irreversible changes. It follows from the experiments that the dipole momentum of the DCM particle was caused by the presence of polar fragments of molecules. The constant dipole momentum of the particles facilitated the aggregation. Based on this, we proposed a model of a structurally inhomogeneous DCM particle.

## 1 Introduction

The technological applications of diamond-containing material (DCM) produced by detonation [1,2] have received interest lately. Chemists, technologists and engineers working with this material have faced difficulties due to heterogeneity of the real powder. DCM particles are known to incorporate several components (such as 4–6 nm diamond grains,  $sp^2$ -carbon, molecular fragments and surface functional groups) [3,4] which are mainly formed via chemical bonding. These particles are also characterized by a complex aggregation [5,6]. From a theoretical point of view, there is considerable difference in the physical and chemical characteristics of the diamond grains and the admixture part of the DCM. Therefore, one can expect that certain conditions of mechanochemical treatment will destroy mainly the non-diamond part. As a matter of fact, conflicting results have been published [5,6] regarding the effects of mechanochemical treatment. Many researchers did not examine the possibility of diamond grain destruction at all, or they did not consider the reasons for this destruction, while the disintegration could increase the total inhomogeneity of the material.

The aim of this work is to study the stability of the diamond grains under mechanochemical conditions.

We suggest two methods that differ in their milling time and their method of transmitting energy to the substance. It should be noted that mechanical milling is likely to produce some amount of disordered carbon in DCM particles; consequently, the study of the DCM structure becomes complicated by the resultant broad D-band competing with the diamond band in the Raman spectra. It is also likely that treatment of this material may cause intensive chemical processes, which introduce further complications because the non-diamond components are systematically identified by different experimental methods [7,8]. To remove these complications, a combination of different research methods is used.

## 2 Experimental

Two types of mills, KM-1 and AGO-2S, were used for the mechanical treatment of DCM particles.

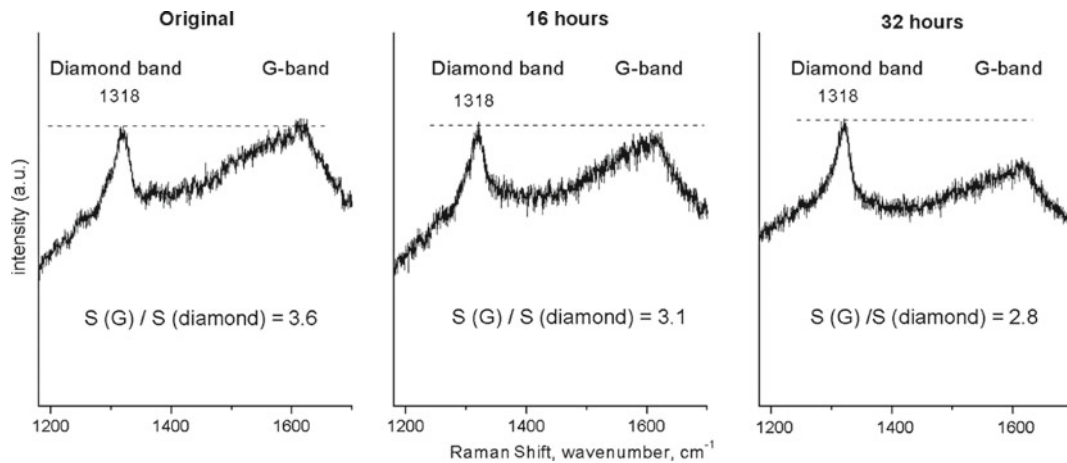
The KM-1 vibration mill had an agate grinding ball with  $d = 47$  mm. The milling times were 12, 16 and 32 h. For the first 2 h the samples were treated at half the maximum vibration amplitude ( $0.5A_{\max}$ ), which was subsequently increased to  $0.75A_{\max}$ .

Stainless steel balls having mass = 100 g and  $d = 8$  mm were used as the grinding media in the AGO-2S planetary mill. The milling times were 5, 15 and 30 min at 2200 revolutions per minute (rpm).

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**Fig. 1.** Raman spectra of the samples treated in the KM-1 mill. The spectra are characterized by two principal bands: the first band, with a maximum in the spectral range  $1315\text{--}1325\text{ cm}^{-1}$ , is a phonon mode of  $F_{2g}$  symmetry (diamond band,  $1333\text{ cm}^{-1}$  for bulk crystal), and the second is a G-band, which identifies  $sp^2$ -carbon. The relative intensity of the G-band depends on the treatment duration. A ratio of the areas of the corresponding bands is shown.

DCM samples used for the milling were synthesized from a trinitrotoluene/hexogen (TNT/RDX) mixture in a carbon dioxide preservation atmosphere and extracted from the detonation soot by thermoxidation in the presence of boron anhydride.

Infrared spectra were obtained in the  $400\text{--}4000\text{ cm}^{-1}$  range using a Tensor 27 (Bruker) Fourier spectrometer. The preparation consisted of 2 mg of DCM mixed with 1000 mg KBr that was pressed into a pellet. The mixing time and the pellet compression pressure were the same for all samples.

Raman spectra were recorded with a T64000 Jobin Yvon spectrometer in the frequency range  $100\text{--}4000\text{ cm}^{-1}$ . The excitation was produced by argon ion laser radiation at  $514.5\text{ nm}$  which delivered  $37\text{ mW}$  of power onto the sample.

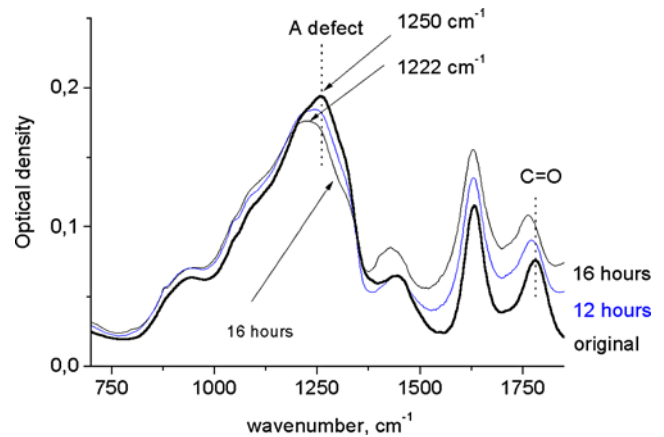
X-ray diffraction (XRD) patterns for the DCM samples were obtained using an XRD-6000 Shimadzu diffractometer.

The size of the particles was measured with a Fritsch Analysette-22 laser analyzer ( $\lambda = 655\text{ nm}$ ,  $7\text{ mW}$  He-Ne laser).

### 3 The effect of treatment in the KM-1 mill

X-ray diffraction patterns for samples treated in the KM-1 mill showed that the mill had not destroyed the diamond grains in the DCM particles. To identify the diamond grains in a DCM particle, the diffraction maxima at  $2\theta = 43.7^\circ$ ,  $75.4^\circ$  related to reflections from the (1 1 1) and (2 2 0) planes were observed for all samples. The mean size ( $d$ ) of the diamond grains was calculated using the Scherrer equation:  $d$  (original sample) =  $5.3\text{ nm}$ ,  $d$  (12-h treatment) =  $5.2\text{ nm}$  and  $d$  (16-h treatment) =  $5.3\text{ nm}$ . Thus, acceptable diamond identification was possible.

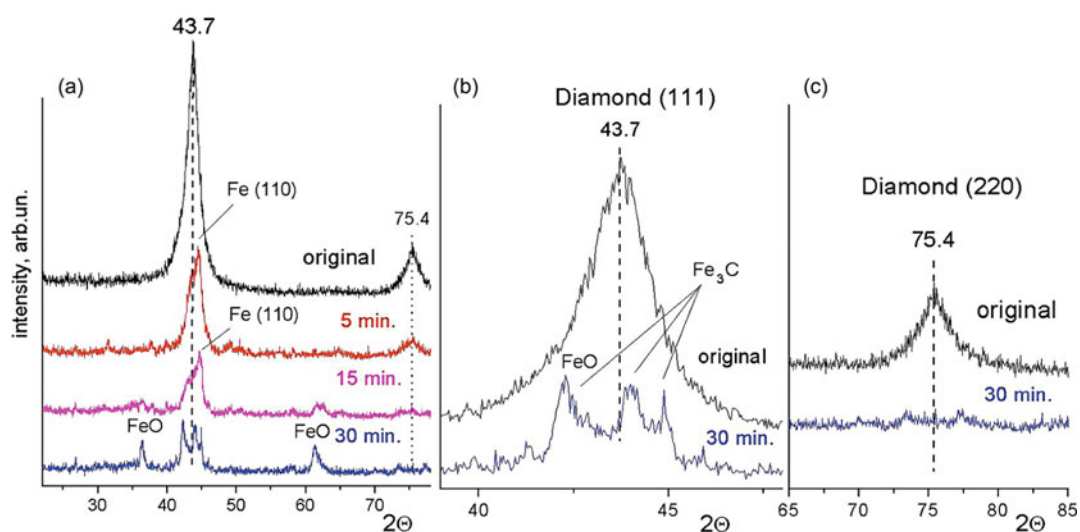
In the Raman spectra of the treated DCM samples, a diamond band with a maximum at  $1315\text{--}1325\text{ cm}^{-1}$  (the phonon mode of  $F_{2g}$  symmetry) and a G-band that



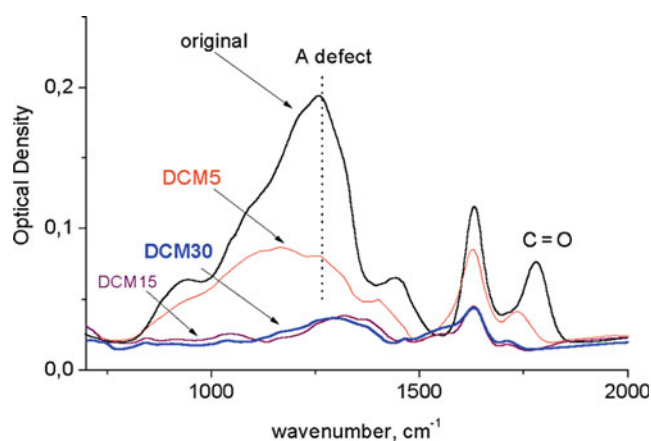
**Fig. 2.** (Color online) IR spectra of DCM samples treated in KM-1 for different periods of time. Absorption in the spectral region  $1000\text{--}1500\text{ cm}^{-1}$  is a superposition of two bands. The stepwise absorption band with the main peak in the spectral range  $1250\text{--}1260\text{ cm}^{-1}$  (nitrogen A defect) is due to the inclusion of two neighboring nitrogen atoms into the diamond grain of DCM. A second contribution to the IR absorption is caused by a C-O stretching vibration ( $1100\text{ cm}^{-1}$ ). Possibly the mechanical treatment caused a local oxidation process, which increased the contribution related to the stretching C-O vibration.

identified carbon domains with  $sp^2$ -hybridization were observed (Fig. 1). The ratio of the respective band areas is shown in Figure 1. The experiment showed that the relative portion of  $sp^2$ -carbon in the DCM samples decreased with the duration of the treatment. The  $sp^2$ -carbon formation is known to be associated with destruction of the diamond domain [4–7]. Therefore, it is reasonable to assume that the  $sp^2$ -carbon domains were located in the immediate vicinity of the diamond grains.

IR spectra of the DCM samples treated in KM-1 over different periods of time were obtained (Fig. 2).



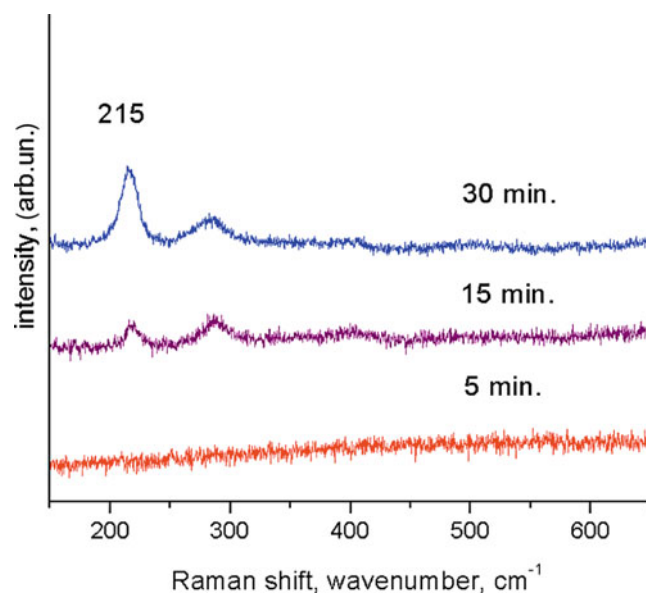
**Fig. 3.** (Color online) XRD patterns for the original sample and the samples after mechanochemical treatment in AGO-2S (a). Diffraction maxima at  $43.7^\circ$  (b) and  $75.4^\circ$  (c) are related to reflections from the (1 1 1) and (2 2 0) planes and identify the diamond grain in the original DCM sample. XRD patterns for DCM30 (30-min treatment) do not allow the diamond phase to be identified.



**Fig. 4.** (Color online) IR spectra of the original sample and the AGO-2S-treated samples DCM5 (5-min treatment), DCM15 (15 min) and DCM30 (30 min). The IR spectra of DCM15 and DCM30 do not show any nitrogen A defect, which can be logically associated with diamond grain destruction in the particles.

The changes in the IR spectra of the treated samples agreed with the results of Mironov et al. [3]. It was suggested that absorption in the spectral region  $1100\text{--}1300\text{ cm}^{-1}$  can be treated as the superposition of two bands. The stepwise absorption band with its main peak in the spectral range  $1250\text{--}1260\text{ cm}^{-1}$  (nitrogen A defect) occurred due to the inclusion of two neighboring nitrogen atoms within the diamond grain of the DCM. A second contribution to the IR absorption was caused by a C-O stretching vibration ( $1100\text{ cm}^{-1}$ ).

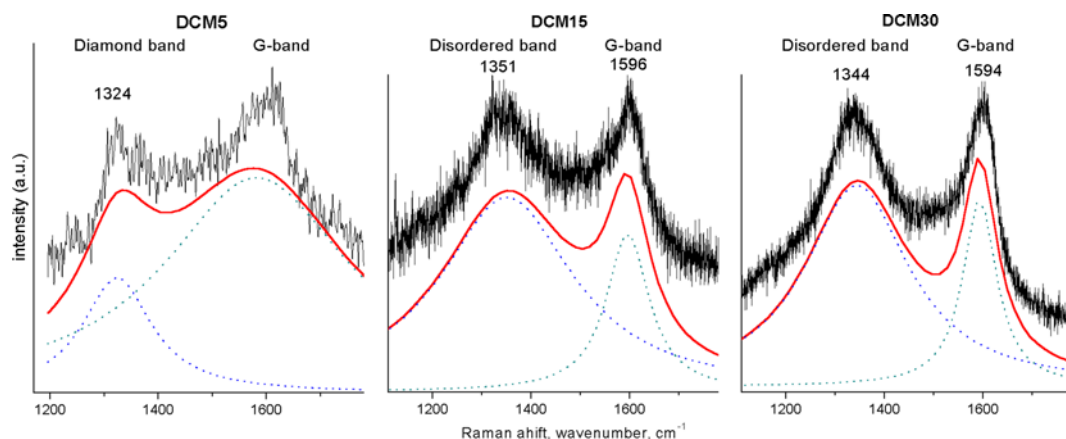
It is possible that mechanical treatment caused local oxidation processes, thus increasing the contribution associated with the stretching C-O vibration. As a result, the maximum absorption was observed at smaller



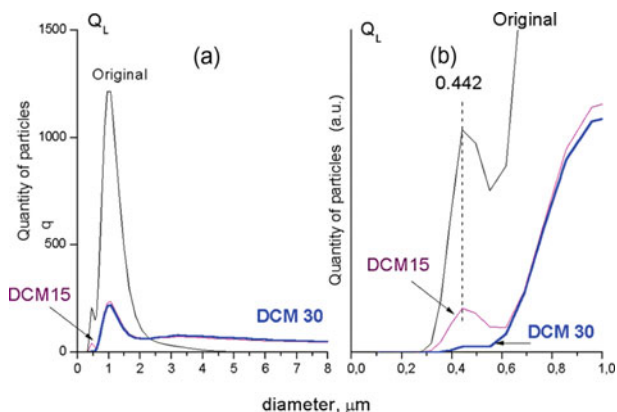
**Fig. 5.** (Color online) Raman spectra of the samples treated by AGO-2S in the region  $100\text{--}600\text{ cm}^{-1}$ . The spectral features ( $215\text{ cm}^{-1}$  and  $286\text{ cm}^{-1}$  bands) indicate the formation of carbon nanotubes. The Raman spectra imply that significant structural changes have occurred in DCM particles.

wavenumbers. In addition, the maximum stretching C=O vibration was observed at  $1763\text{ cm}^{-1}$  (16-h treatment),  $1777\text{ cm}^{-1}$  (original sample) and  $1772\text{ cm}^{-1}$  (12-h treatment) (Fig. 2).

It should be noted that reliable diamond identification was possible with observations of all DCM samples treated in KM-1. Hence, the changes observed in the IR and Raman spectra were most likely related to the surface behavior of the DCM particles. Based on the changes in the Raman spectra, it would be logical to assume that



**Fig. 6.** (Color online) Raman spectra of DCM5, DCM15 and DCM30 treated by AGO-2S in the region 1000–1800  $\text{cm}^{-1}$ . A two-component decomposition of the spectra was performed using the Lorentz equation. The ratio of areas of the corresponding bands was  $S(\text{G})/S(\text{Diamond}) = 5.1$  for DCM5,  $S(\text{G})/S(\text{Disordered band}) = 0.3$  for DCM15, and  $S(\text{G})/S(\text{Disordered band}) = 0.3$  for DCM30. The band in the Raman spectra for DCM15 is characterized by a maximum at  $1351 \text{ cm}^{-1}$ , i.e., it is not a diamond band.



**Fig. 7.** (Color online) Size distribution (based on Mie theory) of the original DCM samples and the milled samples in the region (a) 0–8  $\mu\text{m}$  and (b) 0.2–0.8  $\mu\text{m}$ . Function  $Q_L$  represents a standardized quantity of particles of a relevant diameter. The size distribution curves for DCM15 (15-min treatment), DCM30 (30-min treatment) and the original sample (after ultrasound treatment) are characterized by the same maximum at 442 nm and a double maximum at 957 and 1068 nm. This means that part of the 4–5 nm grains did not undergo a direct mechanical force.

$sp^2$ -carbon was located on the particle surface and near the diamond grains. From the IR spectra, it follows that the DCM particles have a functional cover. The experimental evidence obtained leads to the conclusion that the particle surface is non-uniform.

#### 4 The effect of treatment in the AGO-2S mill

Figure 3 shows the X-ray diffraction patterns for the milled samples. The main peak of diffraction reflection from the (1 1 0) plane of Fe (Im3m) dominates in the XRD patterns for the samples treated for 5 min (DCM5) and 15 min

(DCM15). This implies the occurrence of a mechanical interaction between the ball material and the samples.

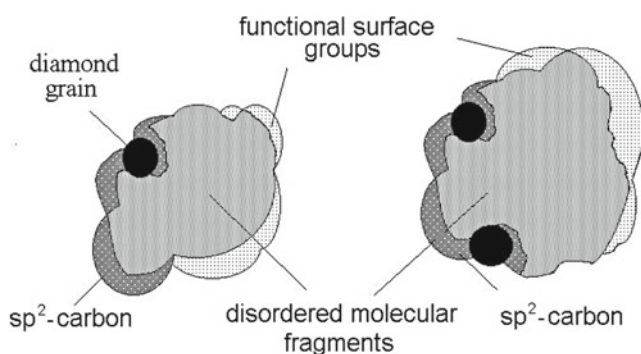
The XRD pattern for the DCM15 sample did not contain a second diamond peak of diffraction reflection from the (2 2 0) plane ( $2\theta = 75.4^\circ$ ). We were not able to identify the diamond phase from the XRD pattern for the sample milled for 30 min (DCM30). The XRD patterns for this sample contained the maxima corresponding to FeO (Fm3m) (diffraction from the (2 0 0), (1 1 1) and (2 2 0) planes) and  $\text{Fe}_3\text{C}$  (Pnma) (diffraction from the (0 3 1), (2 2 0) and (2 1 1) planes). Consequently, chemical processes in DCM15 and DCM30 occurred that destroyed the diamond grains.

Significant variations in the IR spectra of the milled samples were observed (Fig. 4). It was impossible to identify the nitrogen A defect in the IR spectra of DCM15 and DCM30; we attributed this to the destruction of diamond grains in the particles, in agreement with the XRD data. Oxygen-containing groups appeared which were involved in the DCM destruction, since the optical density of the  $1630 \text{ cm}^{-1}$  and  $1777 \text{ cm}^{-1}$  bands was reduced.

Considerable changes were observed in the Raman spectra of the treated samples (Figs. 5 and 6). New bands at  $215 \text{ cm}^{-1}$  and  $286 \text{ cm}^{-1}$  could be explained from the standpoint of carbon nanotube formation (radial-breathing mode or RBM). The tube diameter was estimated based on  $d = 234/w$ , where  $d$  is the tube diameter and  $w$  is the maximum of the radial-breathing mode (RBM) in wavenumbers [9]. In a first approximation, the nanotube diameter (0.8–1.1 nm) [9] could be treated as an estimated thickness of the  $sp^2$ -carbon domain in the original DCM samples.

Figure 6 shows the Raman spectra of the treated samples DCM5, DCM15 and DCM30 in the spectral region 1000–2000  $\text{cm}^{-1}$ . It followed from the experimental spectra of DCM15 and DCM30 that the D (disordered)-band with a maximum at  $1351 \text{ cm}^{-1}$  dominated in that part of the spectra, i.e., the diamond grains were destroyed. The ratio of areas of the principal bands in this spectral





**Fig. 8.** The proposed models of a DCM particle. The DCM particle consists of diamond grain (or grains),  $sp^2$ -carbon, molecular fragments and a surface functional cover. The surface of the particle is non-uniform. The thickness of the  $sp^2$ -carbon layer surrounding the diamond grain is approximately 0.8–1.1 nm.

region is shown in Figure 6. The qualitative change in this value (3.6 for the original sample and 0.3 for DCM15 and DCM30) indirectly proves that structural changes occurred in the particles.

A broad 2D-band with a maximum at around  $2600\text{--}2750\text{ cm}^{-1}$  was observed in the Raman spectra of DCM30. Apparently, the mechanical treatment caused formation of disordered carbon. Thus, the Raman spectra showed that significant structural changes had occurred in the particles. To explain these changes, it was necessary to assume that the DCM particles were based on chemical bonding.

In comparing the treatment results for both mills, it is seen that effective destruction is greatly affected by the method of energy transmission from the mill to the substance. The higher density of energy transmitted to the material through the AGO-2S resulted in high efficiency milling.

## 5 The size measurement

The size distribution curves for all three samples, DCM15 (15-min treatment), DCM30 (30-min treatment) and the original sample (after ultrasound treatment), were characterized by a maximum at 442 nm and a double maximum at 957 and 1068 nm (Fig. 7). This implied that some of the diamond grains (5 nm size) did not undergo a direct mechanical effect. Apparently the mechanical force destroyed the non-diamond part to a larger extent and also initiated some irreversible physical and chemical changes in the particles. The destruction of diamond grains and the formation of disordered carbon domains resulted from these irreversible changes.

The duration of DCM formation in the detonation wave was extremely short (less than  $4\ \mu\text{s}$ ) [10]; therefore, the DCM particles were generally characterized by a high number of defects and had structural reasons to be destroyed. Certainly these structural reasons included a density contrast (which from a thermodynamic standpoint was a significant destabilization factor), relatively

high oxygen content in the elemental composition and the presence of defects in the diamond grains. The nanodiamond defectiveness was extensively discussed lately. In an earlier publication [4] we attempted to estimate the concentration of nitrogen A defects. Evidently the high defectiveness decreased the stability of the diamond grains. We considered that some of diamond grains had been partially destroyed by interacting with the explosion chamber walls. Identification of  $sp^2$ -carbon in DCM particles as a product of  $sp^3$ -grain destruction confirmed this assumption.

Note that the DCM30 sample contained aggregates of the same sizes (957 nm and 1068 nm) as the original sample, although the diamond phase had been destroyed in the sample. This meant that the aggregation was not totally associated with the diamond grains. It is most likely that some of the molecular fragments were polar and together formed a total dipole momentum of the DCM particles. The constant dipole momentum of the particles facilitated the aggregation.

## 6 Discussion

The experiments showed that the DCM homogeneity was dependent on the structure of the DCM primary particles [3, 4, 11]. These particles were built with chemical bonding, and their stability must be examined as a whole. That is, both components (diamond and non-diamond) affected the DCM particle stability. The main reasons a structure formed with this stability mechanism were non-equilibrium physical and chemical conditions, excess of energy [11, 12] and a short formation duration (less than  $4\ \mu\text{s}$ ) [10]. See the discussion in [11, 12] for further details. The secondary processes also influenced the structural heterogeneity of the DCM. During these processes, the diamond grain was able to hinder the oxidation influence on the DCM particle and acted as a frame structure for the entire primary particle. As followed from the experiments, the domain of the molecular fragments (or the non-diamond component) increased the size of the primary particle and consequently enhanced the particle stability. Generally the stability of small crystals depends significantly on their size [13]. The molecular fragments were characterized by a different dimensional dependence.

The experiments showed that the mechanical effect destroyed the non-diamond component, damaged the stabilization mechanism and initiated the irreversible processes. The high defectiveness of the DCM particles decreased their stability. A comparison of the treatment results for both mills suggested that for effective destruction, the method of energy transmission from the mill to the substance was of great importance. Possibly the high density of energy of the milling and the structural heterogeneity of the DCM were the main reasons that the irreversible chemical and physical processes were initiated.

It followed from the experiments that the oxygen-containing groups influenced the stability of the primary particles.

The experiments revealed that the particles had a constant dipole momentum that facilitated the aggregation. This dipole momentum was caused by the presence of polar fragments of molecules.

It is likely that the non-equilibrium conditions of synthesis caused the formation of a set of related DCM structures. Nevertheless, the experiments allowed the introduction of an average particle model. Figure 8 shows the proposed model containing diamond grains. We chose a relatively smooth surface of the particle in the model, whereas the actual surface is fractal-like with some irregularities [14, 15].

A non-symmetric distribution of the main components is typical of a DCM particle, i.e., DCM particles vary in density. As described earlier [11, 12], this distribution is associated with the influence of non-equilibrium detonation processes (density fluctuations) on the synthesis.

## 7 Conclusions

Mechanical milling of the diamond-containing material produced by detonation using KM-1 and AGO-2S mills was performed. Experimental spectra for infrared absorption, Raman scattering and X-ray diffraction patterns were obtained for the treated DCM samples.

Comparison of the Raman and IR spectra for the KM-1 milled samples led us to conclude that the surface of the DCM particles was not uniform.

It followed from the IR spectra and XRD patterns for the AGO-2S milled samples that the mechanical force that resulted from the milling with AGO-2S initiated irreversible physical and chemical changes in the DCM particles and destroyed them. Considerable changes (D-band appearance) which were observed in the Raman spectra of the treated samples confirmed this result.

The size measurement experiments showed that the aggregation was not totally associated with the diamond grains. Consequently the dipole momentum of the structural-heterogeneous particles of DCM was to a greater extent caused by the presence of polar fragments of molecules and facilitated the aggregation. Also it followed from these measurements that the mechanical effect destroyed the non-diamond component of the particles, i.e., the destruction of the non-diamond part initiated these irreversible changes in the particles.

The experiments confirmed that the DCM particles were based on chemical bonding and the DCM stability was defined by the both diamond and non-diamond

components, i.e., the DCM is an independent detonation product consisting of  $sp^3$ -diamond grains, carbon domains with  $sp^2$ -hybridization, molecular fragments and functional groups. The experiments showed that the degree and products of the destruction of the detonation-produced DCM varied according to the type of forcing and the density of energy transmitted.

The obtained results allowed us to introduce an approximate model of a structural-inhomogeneous DCM particle which reflected the influence of the high-temperature processes on the condensation of this material.

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