**Effect of Cyclotrimethylenetrinitramine on the Wet Synthesis of Ultra-nanocrystalline Diamond**

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**Abstract:**
The Ultra-nanocrystalline diamond (UNCD) was synthesized by the detonation of a high explosive mixture in water confinement. The presence of a diamond phase was revealed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). X-ray line broadening (XRLB) was used to evaluate the peak profiles of diamond nanoparticles and their corresponding average crystallite sizes. The micro structure has investigated by high resolution transmission electron microscopy. The results indicate that the optimum of Cyclotrimethylenetrinitramine addition on TNT is 60% and the size of nanodiamond particle was about 5nm.

**Keywords:** Cyclotrimethylenetrinitramine, TNT, Ultra dispersed nanodiamond, wet media

**1- INTRODUCTION**

There is increasing interest in Nanomaterials and nanoparticles about their formation and processing. Specifically, particulate nanodiamond, a fairly new nanomaterial, has unpredicted areas of practical use, from electro rheology to biosensors [1]. There are numerous reports on experimental observations of nanosize diamond [2]. The methods of nanodiamond synthesis are reported diversely involving methods such as a gas-phase nucleation at ambient pressure [3], chlorination of carbide material at moderate temperature [4], HPHT graphite/nanocarbon transformation within shock wave [5,6], and carbon condensation during explosive detonation [7].

In the energy using method from an explosion for diamond production, diamond clusters are formed from carbon atoms contained within an explosive molecules, so only the explosive material is used as a precursor material. A wide variety of materials can be used, a typical explosive is 2-methyl-1,3,5-trinitrobenzene (TNT) composed of C,N,O, and H with a negative oxygen balance.

The number of publications in the literature e.g. [8-10] in which the possible formation of finely dispersed diamond particles during detonation of condensed explosives with a negative oxygen balance is discussed, has recently increased. The most studies have been focused on the explosive decomposition of TNT performed in chambers which were filled with inert gases in order to release the maximum amount of free carbon and prevent the diamond particles from oxidation. Also most previous studies on the detonation synthesis process have been done at military or commercial plants, and thus only limited reports are available for the scientific community. This study discusses the effect of Cyclotrimethylenetrinitramine addition on the detonation synthesis of UNCD in the water media as a coolant.
2- EXPERIMENTAL

Explosive charge was a solid cylinder with 8 cm in diameter and 24 cm in length. The TNT with a density of 1.68 to 1.70 g/cm\(^3\) was mixed with cyclotrimethylenetrinitramine as an explosive material with the weight percent of 0, 10, 20, 30, 40, 50, 60 and 70 wt%. A 30 litters polyethylene water container provides the water blanket around the explosive charge.

After performing the explosion, the condensed detonation product is given sufficient time in a conical sedimentation tank to separate and form a thick black slurry. This slurry is filtered and dried out in an electric drier. The product is a black powder composed of nanodiamond and other carbon component and some traces of metals from container and explosive initiator.

To determine the fraction of nano-diamond in the detonation product, a laboratory procedure using perchloric acid as the oxidizing agent is followed. A double layer glass reactor with hot oil circulation insures proper heating of the product. To complete the batch process, detonation product is kept at 180°C for about 3 hours. After several times washing by Ammoniac, the grey solid particles (UDD) is neutralized. Then it is filtered and dried at 115°C. The weight of this residue is a measure of UDD yield.

Transmission electron microscopy images were obtained using a Philips TEM operating at the voltage of 200 kV. A conventional powder diffractometer Philips 1730 (with Philips APD) using Cu K\(\alpha\) radiation 1.5418 Å operated at 40 kV and 30 mA and pyrolitic graphite secondary monochromator was used to obtain the X-ray spectra of the samples.

X-ray diffraction analysis method provides information not only on particle dimensions but also on average sizes of coherently scattering domains, which we refer to as crystallites. For X-ray diffraction peak profile analysis, the (111) peak of diamond (I=100) is used. This peak is treated to analyzed and provided information on the average crystallite size of diamond nanoparticles. The value obtained by x-ray line broadening technique (XRLB) is comparable with the one obtained from TEM images.

3- RESULTS AND DISCUSSION

The results which obtained using different amounts of Cyclotrimethylenetrinitramine in water media show the yield of UNCD and condensed carbon (CC) relative to the initial TNT (Table 1). At the same mass of explosive, the highest yield is observed by TNT-Cyclotrimethylenetrinitramine ratio (TCR) of 40/60.

Previous studies showed that during the detonation of TNT, its recorded data in Chapman-Jouguet plane where the chemical reactions have basically been completed, the pressure is 18 Pascal and the temperature is between 3000-4000 K, which corresponds to the region of stability of the diamond phase [11] while no appreciable yield of diamond was obtained during the detonation of TNT. More powerful compositions, which increased the pressure and temperature, which appreciable yield of UNCD in a detonation of an explosive. The simplest of those is a mixture of TNT with Cyclotrimethylenetrinitramine.

By increasing the explosion pressure, detonation soot contains the higher percent of nanodiamond particles [12]. Its reasons have been discussed in Refs. [13,14] on the basis of the diamond-graphite pressure-temperature (P-T) phase diagram.

Figure 1 shows the transmission electron microscope (TEM) images of synthesised diamond nanoparticles under optimal TCR (60% Cyclotrimethylenetrinitramine, 40% TNT). It can be seen that the nanoparticles are in spherical shapes. The size measurement on the electron micrographs gives the values in the range of 3-12 nm, with an average size around 5 nm. Figure 2 shows diffraction pattern of nanodiamond particles. The corresponding electron diffraction patterns showed the reflection rings characteristic of essentially randomly oriented diamond grains. The diffraction rings were quite diffuse because of the nanosize of the particles.

The XRD analysis is shown in Figure 3(a) reveals the synthesized diamond nano powder with crystalline structure, in addition to some amorphous content and organic materials. Figure 3(b) shows the X-ray diffraction of the same sample after washing process. By comparing the peak surfaces of the region 15°-
Table 1: Yield of Ultra-nanocrystalline diamond and condensed carbon from different amount of TNT-Cyclotrimethylenetrinitramine ratio in controlled water media

<table>
<thead>
<tr>
<th>Cyclotrimethylenetrinitramine (wt%)</th>
<th>CC/explosive (wt%)</th>
<th>UNCD/explosive (wt%)</th>
<th>UNCD/CC (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>13.93</td>
<td>2.11</td>
<td>15.15</td>
</tr>
<tr>
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<td>13.74</td>
<td>6.55</td>
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<td>7.80</td>
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</tr>
<tr>
<td>70</td>
<td>12.86</td>
<td>6.28</td>
<td>48.83</td>
</tr>
</tbody>
</table>

Figure 1: Typical electron micrographs of synthesised nanodiamond
Figure 2: The electron diffraction pattern of cubic diamond.

Figure 3: X-ray diffraction of the synthesized diamond nanopowder (a) before and after washing process.
45° 0, it is seen that there were more nano-diamond and less organic materials or graphite inclusions in the diamond particle.

4- CONCLUSION

The following conclusions can be made from this study:

(1) Optimal TNT-Cyclotrimethylenetritramine ratio (TCR) for synthesizing nano-diamond particles is 40/60 (60% Cyclotrimethylenetritramine, 40% TNT).

(2) Typical HRTEM electron micrographs of synthesised diamond particles under optimal TCR were confirmed nanocrystalline diamond powder (NDP) with particle diameters of 3-12nm. The particles are roughly spherical in shape and are typically coated with a graphitic monolayer. The corresponding electron diffraction patterns showed reflection rings characteristic of essentially randomly oriented diamond grains. The diffraction rings are quite diffuse because of the nanosize of the particles.

References


