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Effect of Cyclotrimethylenetrinitramine on Wet Synthesis of Ultra-Nanocrystalline Diamond

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The ultra-nanocrystalline diamond was synthesized by the detonation of a high explosive mixtures in water confinement. The presence of a diamond phase was revealed by X-ray diffraction and transmission electron microscopy. X-Ray line broadening was used to evaluate the peak profiles of diamond nanoparticles and their corresponding average crystallite sizes. The micro structure of nanocrystalline diamond have been investigated by high resolution transmission electron microscopy. The results indicate that the optimum of cyclotrimethylenetrinitramine addition on 2-methyl-1,3,5-trinitrobenzene is 60 % and the size of nanodiamond particle was about 5 nm.

Key Words: Cyclotrimethylenetrinitramine, 2-Methyl-1,3,5-trinitrobenzene, Ultra dispersed nanodiamond, Wet media.

INTRODUCTION

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

In the method of using energy from an explosion for diamond production, diamond clusters are formed from carbon atoms contained within in explosive molecules themselves, 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 papers in the literature[8-10] in which the possible formation of finely dispersed diamond particles during detonation of condensed explosives with a negative oxygen balance has recently increased. Most of the papers have been focused on the explosive decomposition of TNT performed in chambers which

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were filled with inert gases in order to release the maximum amount of free carbon and prevent the diamond particles from being oxidized. Most of the previous studies on the detonation synthesis process have also been done at military or commercial plants and thus only limited reports are available for the scientific community. This studies report the effect of cyclotrimethylenetrinitramine addition on the detonation synthesis of ultra-nanocrystalline diamond in water media as a coolant.

EXPERIMENTAL

Explosive charge was a solid cylinder (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 0, 10, 20, 30, 40, 50, 60, and 70 wt % cyclotrimethylenetrinitramine used as explosive material. 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.

For determining 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. Detonation product is kept at 180 ºC for *ca.* 3 h for completion of the batch process. The grey solid particles that are ultra dispersed diamond is neutralized after washing it several times by ammoniac and is filtered and dried at 115 ºC. The weight of this residue is a measure of ultra dispersed diamond 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 CuK_α 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 transmission electro microscopy (TEM) images.

RESULTS AND DISCUSSION

The results obtained using different amount of cyclotrimethylenetrinitramine in water media showed that the yield of ultra-nanocrystalline diamond and condensed carbon (CC) relative to the initial TNT (Table-1). For the same mass of explosive the highest yield is observed by TNT cyclotrimethylenetrinitramine ratio (TCR) of 40/60.

TABLE-1
YIELD OF ULTRA-NANOCRYSTALLINE DIAMOND AND CONDENSED CARBON FROM DIFFERENT AMOUNT OF TNT-CYCLOTRIMETHYLENE-TRINITRAMINE RATIO IN CONTROLLED WATER MEDIA

Cyclotrimethylenetrinitramine (wt %)	CC/explosive (wt %)	UNCD/explosive (wt %)	UNCD/CC (wt %)
0	13.93	2.11	15.15
10	13.84	3.86	27.89
20	13.76	5.20	37.79
30	13.74	6.55	47.67
40	12.97	6.43	49.57
50	13.01	7.72	59.34
60	13.05	7.80	59.77
70	12.86	6.28	48.83

Previous studies showed that during the detonation of TNT, its recorded data in Chapman-Jouguet plane, where the chemical reactions have basically been completed, are P = 18Pa and T = 3000-4000 K, which corresponds to the region of stability of the diamond phase[11]. But 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 ultra-nanocrystalline diamond in a detonation of an explosive. The simplest of these compositions is a mixture of TNT with cyclotri-methylenetrinitramine.

It was shown[12] by increasing explosion pressure, detonation soot contain higher percent of nanodiamond particles. The reasons for that have been discussed by earlier workers[13,14] on the basis of the diamond-graphite pressure-temperature (P-T) phase diagram.

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

The XRD analysis reveals the synthesized diamond nano powder with crystalline structure, in addition to some amorphous content and organic materials. The X-ray diffraction of the same sample after washing process have also studied. By comparing the peak surfaces of the region 15º-45º 2θ, it is seen that there was more nano-diamond and less organic materials or graphite inclusions in the diamond particle.

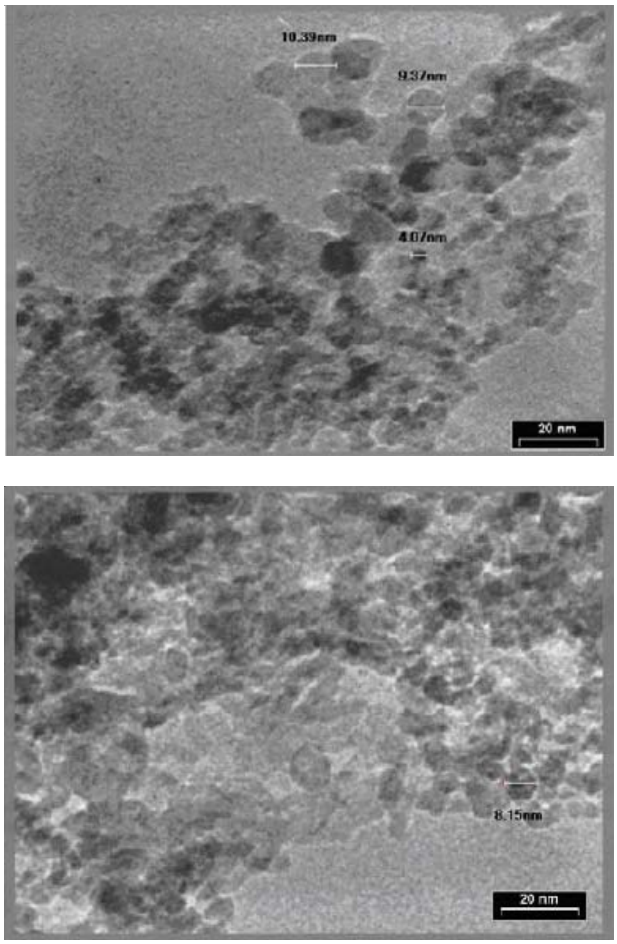

Fig. 1. Electron micrographs of synthesised nanodiamond

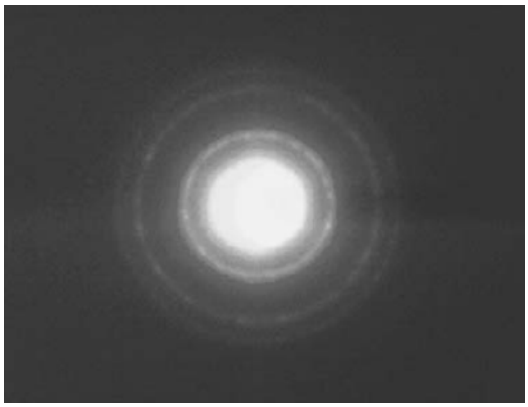

Fig. 2. Electron diffraction pattern of cubic diamond

Conclusion

The following conclusions can be made from this study: (1) Optimal TNT-cyclotrimethylenetrinitramine ratio (TCR) for synthesizing nanodiamond particles is 40/60 (60 % cyclotrimethylenetrinitramine, 40 % TNT). (2) Typical HRTEM electron micrographs of diamond particles synthesised under optimal TCR was confirmed nanocrystalline diamond powder (NDP) with particle diameters of 3-12 nm. The particles are roughly spherical in shape and they were typically coated with a graphitic monolayer. The corresponding electron diffraction patterns showed reflection rings characteristic of essentially randomly oriented diamond grains. The diffraction rings were quite diffuse because of the nanosized of the particles.

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