Diamond & Related Materials 54 (2015) 59–63

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Detonation of nanosized explosive: New mechanistic model for nanodiamond formation

V. Pichot *, M. Comet, B. Risse, D. Spitzer

NS3E "Nanomatériaux pour les Systèmes Sous Sollicitations Extrêmes" UMR 3208 ISL/CNRS/UdS, French German Research Institute of Saint-Louis (ISL), 5 rue du Général Cassagnou, 68301 Saint-Louis, France

ARTICLE INFO

Available online 2 October 2014

Keywords:
Detonation nanodiamond
Nanostructured explosive
Formation mechanisms
Nucleation sites

ABSTRACT

While nanodiamonds are synthesized by detonation of microstructured explosives since 50 years ago, we developed a novel approach to synthesize these particles by using nanostructured explosives. This new synthesis method leads to novel results not only in the control of the size, but also in the understanding of the nanodiamond synthesis and the detonation mechanisms. The use of explosive particles with size down to 40 nm results in the formation of detonation nanodiamonds with a mean size of 2.8 nm. In the light of these experiments, a model based on the size of the material involved during the detonation process has been developed to explain the size of the obtained nanodiamond. According to hypotheses based on the number of the nanodiamond nucleation sites, the experimental results are in favor of a decrease in the size of the nanodiamonds formed when the size of the explosive particles used during detonation is decreased.

1. Introduction

Diamond particle formation during the detonation process has been investigated for a long time [1–4], and different hypotheses on their formation were developed based on thermodynamical calculations [5,6], Small Angle X-ray Scattering measurements [7,8]. These studies allowed obtaining valuable information on the place and moment at which the nanodiamonds form.

The explosive molecules mainly decompose and the carbon atoms which are not transformed into CO or CO_2 crystallize into very small aggregates due to droplet coalescence or aggregation of carbon radicals. However, these results were always considered from detonation experiments conducted with microstructured explosive charges which do not have a homogeneous composition at the nanodiamond formation scale. The decrease in the size of the explosive particles which are used for the synthesis of nanodiamonds should allow us to better understand the formation mechanisms of these particles and moreover, their size dependence with respect to the available carbon atoms. The consideration of the number of nucleation sites can also give some valuable information.

A very recent study [9] was carried out comparing nanostructured with microstructured explosives and showed that, by using the same explosive compositions and charge densities, smaller nanodiamonds are obtained from nanosized explosives. The particle size distributions of the TNT used as carbon source in this study were centered around 100 nm. From these experiments, it was shown that for explosive particles having a size greater than 200 nm, the size of the synthesized nanodiamond particles did not change from the one obtained from classical microstructured explosives. However, one question remained about the evolution of the size of the synthesized nanodiamonds for TNT particles having a size below 100 nm: is it still possible to continue to decrease the size of the nanodiamond particles synthesized from TNT particles?

In this article, novel experimental conditions are reported by using an octolite component in which the TNT particle size is lower than in the previous studies. These new experiments have led us to propose a new modeling of the nanodiamond formation during the detonation.

2. Material and methods

Nanostructured octolite (octogen (HMX)/trinitrotoluene (TNT)) was prepared according to a unique process which was developed in our laboratory, namely the spray flash-evaporation process [10,11]. The nanostructured explosives were prepared from a 1 wt.% acetone–explosive solution. The acetone–explosive solution under a 40 bar overpressure was atomized into a chamber kept under dynamic vacuum (5 mbar) through a hollow cone nozzle. The temperature of the nozzle was kept constant at 160 °C. The temperature and pressure drop when entering the atomization chamber lead to nearly instantaneous evaporation of the acetone contained in the droplets and to the crystallization of the components. The crystallized explosive particles are then recovered. According to a previous study performed on the optimization of nanohexolite pellets for the synthesis of nanostructured explosive charges, octolite pellets were prepared by compression of octolite powder at 800 bar and 60 °C for 10 min. The explosive charge was made by assembling five pellets cemented together with pyrotechnic glue.

* Corresponding author at: French-German Research Institute of Saint-Louis, 5, rue du général Cassagnou, 68301 Saint-Louis, France.

http://dx.doi.org/10.1016/j.diamond.2014.09.013
0925-9635/

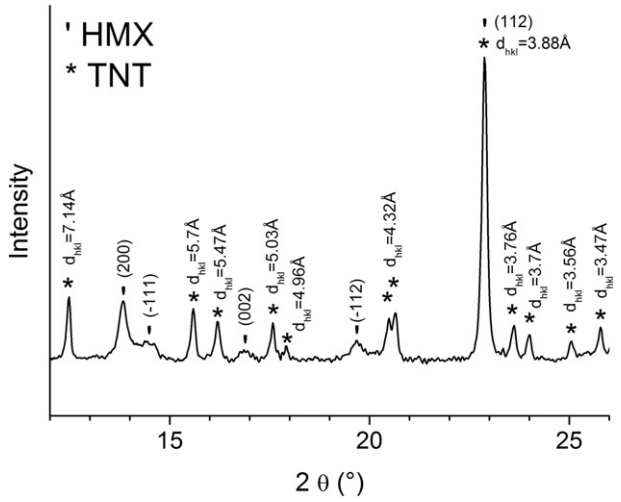

Fig. 1. XRD pattern of nanostructured octolite, lines and stars correspond to HMX (PDF number 00-044-1621) and TNT [12] signals respectively.

The detonation experiment was carried out at the French–German Research Institute of Saint-Louis (ISL) in a detonation chamber. The detonation was initiated by a detonator placed in a booster glued with the explosive charge. The detonation soot was then collected by rinsing the wall of the chamber with deionized water. Further filtration and drying steps were conducted to obtain the resulting detonation powder.

Atomic Force Microscopy (AFM) was performed in tapping mode with a Nanoscope IV multimode AFM (Digital Instruments, Santa Barbara, USA). The probe used was a RTESP (Rotated Tapping Etched Silicon Probe) produced by NanoWorld Ltd. Co., its tip radius is around 8 nm. X-ray diffraction (XRD) was performed on a Bruker D8 Advance powder diffraction spectrometer with Cu $K\alpha_1$ radiation (λ = 0.154 nm). Transmission Electron Microscopy (TEM) micrographs were obtained with a Philips CM200. High Resolution Transmission Electron Microscopy (HRTEM) micrographs were obtained with a JEOL microscope ARM 200 cold-FEG. XRD was performed on a Bruker D8 Advance powder diffraction spectrometer with Cu $K\alpha_1$ radiation (λ = 0.154 nm).

3. Results

The synthesized octolite explosive component was characterized by using XRD and AFM. The XRD pattern (Fig. 1) shows diffraction peaks which come from both HMX and TNT.

The AFM image shows the homogeneous size of the synthesized explosive particles (Fig. 2a), this technique is particularly adapted to the observation of nanostructured explosives as it does not modify the sample on the contrary to SEM for which the electronic beam and the vacuum condition leads to the degradation of the material. The size distribution of the explosive particles was estimated from AFM images by using image J software, more than 1000 particles were analyzed, as the particles are in contact, the particle shapes were defined by segmentation of the image. This distribution curve can be compared to another nanostructured explosive (hexolite (hexogen/trinitrotoluene component)) that has been previously studied (Fig. 2b) [9]. The nanostructured octolite used in this study exhibits a smaller mean particle diameter (49 nm, 95% confidence interval: 4 nm) than previously used nanostructured particles (119 nm, 95% confidence interval: 4 nm).

As shown in a previous study [9], the nanodiamond synthesis from this new explosive composition should give new insights into the comprehension of the formation of the carbon crystallites.

An explosive charge was produced with pellets pressed at 800 bar at 60 °C. While the melting point of TNT is about 81 °C, these experimental conditions allowed maintaining the nanostructuration of the explosive after compression. The density of the explosive charge was measured to be 1.76 $g \cdot cm^{-3}$. After the detonation of the explosive charge, the resulting detonation soot was analyzed by TEM experiments.

The TEM micrographs (Fig. 3) show the typical morphology and size of the nanodiamond particles. The size distribution of the nanodiamonds has been established from TEM. The size of more than 1000 particles was manually measured, by using the Image J software, on individual particles located on the edges of aggregates from more than 40 different TEM micrographs. The distribution curves were obtained from the measured diameters and fitted with a lognormal function.

The size distribution curves obtained from the different nanodiamonds synthesized with octolite and hexolite 60/40 (Fig. 3b) clearly show that the size of nanodiamonds decreases with the size of explosive particles. Ultrasmall nanodiamonds with a mean diameter of 2.8 nm (95% confidence interval: 0.1 nm) prevail when using explosive particles of 40 nm against a mean diameter of 4.2 nm (95% confidence interval: 0.1 nm) for explosive particles of 100 nm. Microstructured explosives lead to the formation of nanodiamonds with a mean diameter of 6.2 nm (95% confidence interval: 0.3 nm). Small fringes that can be seen on HRTEM micrographs reveal the diamond nature of the particles as they are separated by a distance of 2.02 Å which corresponds to the distance between (111) planes of diamond (Fig. 4). It can be noticed that some graphitic shells surrounding the nanodiamonds are present, and this might be due to the buckydiamond structure of the nanodiamonds as referenced in literature [13,14] or to small graphitic layer impurities present in the sample. X-Ray diffraction

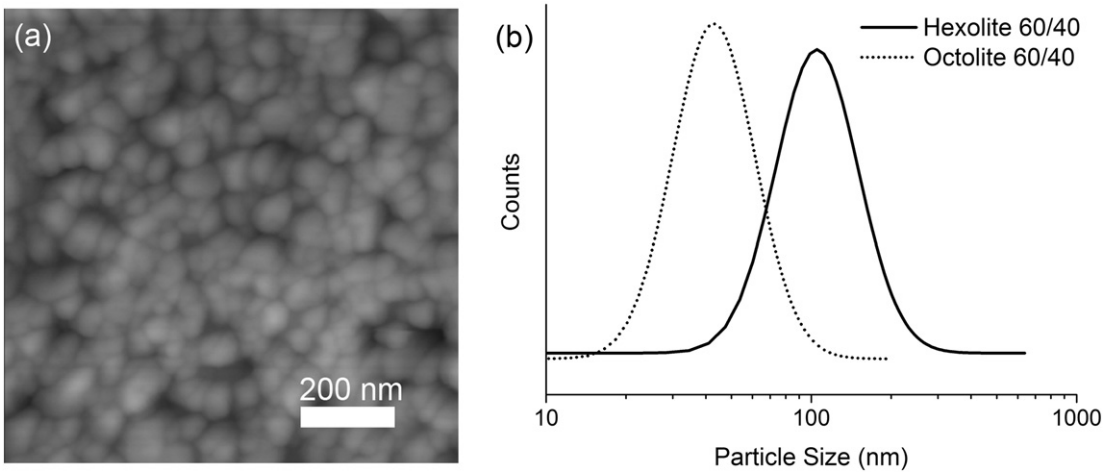

Fig. 2. (a) AFM image obtained on nanostructured octolite, (b) size distribution curves of nanostructured 60/40 hexolite and 60/40 octolite.