Polydispersed Detonation Nanodiamond and Approaches for its Fractioning

I.Petrov[1], P.Detkov[1], J.Walch[2], O.Shenderova[2]

[1]Scientific and Industrial Company "New Technologies", Chelyabinsk 454038, Russia, newtec@chel.surnet.ru
[2]International Technology Center (ITC), Raleigh, NC 27715, USA, oshenderova@itc-inc.org

ABSTRACT

While primary particles of detonation nanodiamond (DND) are within the 2-10nm size range, during the synthesis and purification processes DND aggregates up to several microns are typically formed. Tightly- and loosely-bond aggregates originate from chemical and Van-der-Waals types of bonding between primary particles. In this paper, industrial methods of disaggregating DND product using specific ultrasonic treatment followed by fractioning will be discussed. Importantly, the demonstrated approach of combining ultrasonic treatment with centrifugation avoids contamination of the final DND product.

Keywords: detonation nanodiamond, aggregates, fractions, ultrasonic treatment

1 INTRODUCTION

Nanodiamond of detonation origin, so called detonation nanodiamond (DND), invented more than four decades ago [1] gradually has become a popular material in both research laboratories and industrial applications. While several nanodiamond vendors provide both nanodiamond powders and solutions to end users, this unique material still has not penetrated appreciably into any specific market, especially in the USA. A major roadblock in applications of DND is their high agglomeration, so that instead of nano-entities very often end-users work with microscopic-sized particles.

It is well known that primary (monocrystalline) DND particles have narrow size distributions with an average particle size within the 3-5nm range [1]. However, during synthesis, purification and drying of the product, tightly and loosely-bond aggregates are formed. In addition to carbon-related bonding, the presence of different types of metallic and non-metallic impurities facilitates aggregation. Thus, a certain level of purification is required in order to develop aggregate-free DND product.

Recently several approaches of surface modification of DND particles have been developed resulting in suspensions with DND sizes in the range of several tens of nanometers. High temperature graphitization in nitrogen followed by air oxidation is one approach that has been reported in [2]. The DND prepared by this method and suspended in water by sonication had sizes less than 50nm. So called mechanochemical treatment consisting of high-speed shear stirring, high energy ultrasonic or vibration milling in the presence of dispersants was developed by Xu et al. [3,4]. DND slurries in oil with an average particle size of 55nm were prepared using as a dispersant a block copolymer with $-NH_2$ as an anchoring group and a polyester chain as the oil-solvatable block [3]. Aqueous suspensions of DND with an average particle size of less than 40-60nm were prepared using sodium oleate as a dispersant [4]. In another approach, using a stirred-media milling technique, the authors were able to deagglomerate DND down to about several nanometers [5]. DND with very small aggregate size (40-60nm) and very high stability against sedimentation was developed by modification of DND surface [6]. The modified DND [6] can be dried from suspension and resuspended without aggregating. However, the methods described above either require surfactants, or introduce inorganic impurities from the ball milling media or from the modification process. For a variety of applications such product contamination might be acceptable, but development of methods avoiding DND contamination would be beneficial for a variety of applications including the use of DND as biological carriers and markers and in microelectronics with the strict requirement on material purity, etc.

In the current approach, we apply ultrasonic energy to disperse or break loosely-bond aggregates and partially tightly-bond aggregates followed by fractioning. Since every fraction will correspond to a specific size range it is useful for specific niche applications; once fractioned all of the initial polydispersed powder can be used. However, one purpose of the approach was optimization of the ultrasonic treatment regimes resulting in the highest yield of the fraction with the smallest average particle size. While nanodiamond fractioning resulting in more narrow particle size distributions with a range of average particle sizes for different fractions was successfully applied in galvanic coatings in late 90s [7,8], fractioning became a common practice of vendors relatively recently [9]. Also, a method of additional on-site purification using ion-exchange resins had been demonstrated to be beneficial for reducing the metallic impurity content namely Fe and Cr [10]. This scheme (ion-exchange resin purification and fractioning combined with ultrasonic dispersion) became a common practice at *New Technology, Inc*., a detonation nanodiamond vendor.

2 MATERIALS AND METHODS

DND used in the present study was synthesized from a mixture of TNT/RDX (40/60 wt%) explosives using ice cooling media[11]. For production of the detonation soot 1.2 kg of the explosive mixture was loader into a 2 m^2 explosion chamber. Soot produced by this method has been shown to yield 75-80%, of the diamond phase [11]. The high yield decreases the expenses of DND production since it requires less extensive purification, as well as decreases the amount of non-carbon impurities. Two types of soot purification had been used, resulting in two different DND products, namely using acid-chrome anhydride treatment [12] (Ch-St DND) as well as purification in an ozone-flow reactor developed at *New Technologies, Inc*. [13] (Ch-Oz DND). The method of using ozone as the oxidizer is more economical and environmentally friendly than 'wet' chemistry methods. This method allows the production of powder with a minimum content of non-diamond carbon [14].

A method of DND dispersion by means of an ultrasound for galvanic processes was developed and patented in 1996 [15]. It was demonstrated that deagglomeraion of DND only took place in the ultrasonic regime that induced cavitation. If the regime of ultrasound treatment is not optimized, the treatment can result in the absence of DND dispersion, in further agglomeration or even complete coagulation of the entire sample in the suspension. Since standard equipment for such processes was not efficient for obtaining suspensions stable for a long period of time, *New Technologies, Inc* developed an ultrasound system specifically for the dispersion of DND, that consist of a magnetostrictor transducer and a water-cooled ultrasound horn that is directly immersed in the sample. The ultrasound frequency is 20-22 kHz; the output power from the horn can be varied between 100W and 400W. The optimum regime is obtained by frequency tuning using a resonance regulator for each sample, since the sample volume and characteristics of every suspension to be treated vary. Suspensions with volumes up to 1 liter can be treated.. The dispersion of dry DND in water, butyl acetate, acetone, gasoline and other liquids resulting in long-lasting stable suspensions and gels have been successfully demonstrated. For comparison, sonication was also carried out using a sonicator equipped with a tapered titanium horn with a 3mm tip diameter (Cole-Parmer® 750-Watt Ultrasonic Homogenizer EW-04711-60, 20 kHz) that is directly immersed in the sample. Output power is 10W, output intensity ~100W/cm^2.

Industrial-scale centrifuged used for the fractioning was performed using a OS-6M centrifuge (Russia), containing four 700ml swinging buckets; rotor radii 22cm. Laboratory-scale centrifugation was performed at *ITC* using a *Thermo* Multi (RF) Series Multipurpose Centrifuge with fixed angle rotor (8-place x 50ml); maximum rotor radii 17.5 cm.

The nanodiamond powders were treated with a KU 8-2 cation-exchange resin (CER), that results in ~100% removal of Fe impurities and 30% reduction of Cr impurities. Besides, Ch-St powder was additionally gas-phase oxidized in a variety of experiments.

Investigations of the DND size distributions were performed at *ITC* using photon correlation spectroscopy using a Beckman-Coulter N5 Submicron Particle Size Analyzer that is capable of determining particle size distributions in the 3-3000 nm size range. Several categories of the data representations are available. Unimodal intensity-based distribution yields mean particle size and standard deviation. These values are very reproducible from test to test for a particular DND type and are very reliable sample 'signatures'. However, DND as a rule is polydispersed material and more detailed analysis of particle size distributions is required. The polydispersed size distribution can be reported in terms of scattered intensity, particle number, or volume (equivalent to mass); the latter is the most common representation.

3 DND FRACTIONING AND DISPERSION

3.1 Regimes of Fractioning

Similar to material from other DND vendors, commercial powders of Ch-St and Ch-Oz are polydispersed, with an average particle size in water suspensions after sonication of about 250-300 nm and 200 nm for the Ch-St and Ch-Oz DND, correspondingly. First, the effect of additional purification utilizing cation-exchange resin as well as ultrasonic treatment on the yield of the fractions was studied. The centrifugation scheme using the industrial centrifuge was the same in all experiments: G force 13,600xg and fixed centrifugation time for every fraction. Fractions F1-F5 are residues and the fraction F6 is a supernatant from the 5th centrifugation regime (Table 1).

Sample	Centri-fugation, at 13,800g in minutes	Unimodal analysis, size (nm)	Multimodal Intensity Analysis peaks, size (nm)
Poly-dispersed	-	250	160/200/600/1500
F1	3	300	200/800/1500
F2	5	280	180(50%)/700(50%)
F3	10	240	90/100/160/300/350
F4	20	210	130(40%)/320(60%)
F5	40	190	75(23%)/240(77%)
F6	supernatant	180	66(6%)/195(94%)

Table 1. *Centrifugation time for different fractions as well as average particle sizes in different fractions for Ch-St CER fractioned in combination with ultrasonic treatment. Dried powders of different fractions had been resuspended and sonicated 3min usingt the Cole-Palmer Homogenizer before the particle size measurement.*

Figure 1 illustrates the yield of each fraction for different treatments. All of the DND has sedimented following the 5th centrifugation round for the untreated suspensions of the Ch-St, so that there is no F6 fraction. When Ch-St was ultrasonically treated at 400W output power up to 15min, the yield of F6 was 15wt% (this regime is not shown in Fig.1). When Ch-St was additionally purified with the cation-exchange resin (Ch-St CER, Fig.1), but no sonication was applied, the F6 yield was 5wt%. The highest yield of the F6 fraction (more than 50wt%) was achieved using a combination of the CER purification with ultrasonic treatment and gas phase oxidation (Fig.1). The average sizes of the fractions are summarized in Table 1, based on intensity analysis. In volumetric representation, average particle size for F6 is 130nm. The dried fraction F6 has a very dark-grey color.

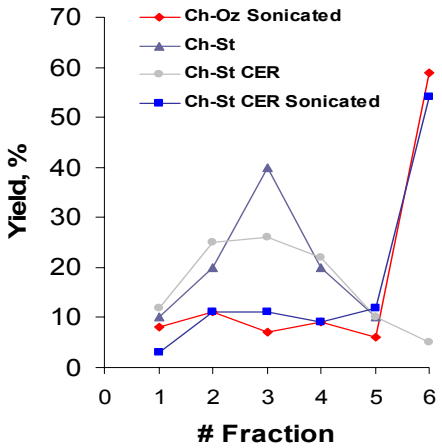

Figure 1. *Yield of different fractions after centrifugation at 13,600xg and time durations from Table 1 for the DND water suspensions.*

Ch-Oz was not treated with CER, since the impurity content is low in the commercial powder [14]; it posses very high sedimentation stability and can be separated into fractions with high yield for the smallest fractions. As a rule, obtaining narrow fractions with small particle sizes for the highest fractions is a prerequisite for high sedimentation stability. F6 fraction for the Ch-Oz is black in color. Thus, according to Fig.1 ultrasonic treatment is an important step during DND fractioning.

In a series of experiments using the laboratory-scale *Thermo* centrifugation system, Ch-St gas phase oxidized material was separated into 8 fractions (Fig.2). In this set of experiments, the G force was varied using the same time of centrifugation for different fractions (5min). Starting with 200ml of 2wt% of Ch-St water suspension sonicated for 5min at an output power of 100W, the smallest fraction with 60nm unimodal size and 0.6 wt.% in the supernatant was obtained. The yield of black fractions (Fr5-Fr8) was approximately 30wt%. Resuspended fractions fourth to seventh, as well as the fraction Fr8 (the supernatant) were stable for at least 3 weeks (until the time of the paper submission).

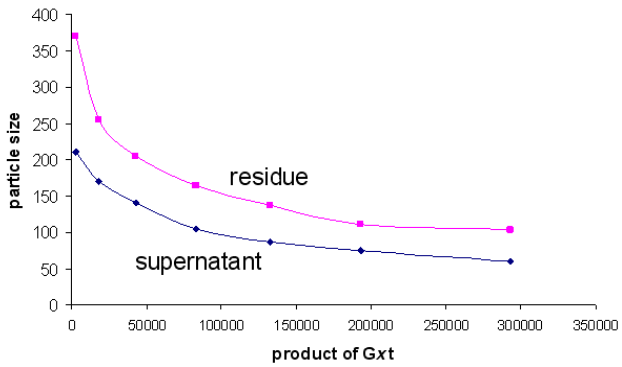

Figure 2. *DND particle size in the supernatant and residue after each centrifugation cycle as a function of centrifugation regimes (integrated G force by time product).*

3.2 Regimes of Ultrasonic Treatment.

Comparative studies of the role of sonication in obtaining stable DND water suspensions using the 'conventional' Cole-Palmer sonicator (4ml sample volume) and the custom build sonicator with magnetorestrictive ultrasonic head (50ml sample volume) were performed. The results are summarized in the Table 2 below. Sonication was performed for 0.1 wt.% of Ch-St. In these experiments Ch-St was not processed with the gas phase oxidation (thus had low sedimentation stability).

Table 2. *Unimodal DND size and sedimentation stability for DND suspension in water under different ultrasonic treatment regimes. Power intensity is output power divided by the area of the horn tip. Dose is total energy injected to the system per unit volume.*

Regime of sonication	size, nm	Sedimentation stability*		Power Intensity, W/cm^2	Dose, J/ml
		in 42hrs	64 hrs		
400W output					
30sec	245	H(268nm)	H/M	338	240
1min	244	M(573nm)	M/L	338	480
200W output					
1min	350			169	240
6min	222	M(538nm)	M/L	169	1440
100W output					
1min	315			85	120
1.5min	277			85	180
6min	217	H(302nm)	H/M	85	720
~10W output					
5min	390	L	L	~135	580
15min	460	L	L	~135	1700

* Notation for sedimentation stability: high (H) – entire sample is opaque, medium (M) – transparency varies along sample height, low (L) – DND completely sediment.

It can be seen from the Table 2 that particular sonication regimes of the powerful sonicator improve both particle dispersivity (smaller size are detected) and suspension stability. It is important to note, that if the sonication time is longer than optimum, the negative effect of increased particle agglomeration can be the result (last line in Table 2).

3.3 DND of Ozone Purification.

In addition to excellent sedimentation stability in water suspensions, high sedimentation stability has been demonstrated for Ch-Oz as well as its fractions in a variety of organosols (fig.3). The black fraction of Ch-Oz can be dispersed (up to several wt%) in 1-methyl-2pyrrolidinone, which is a solvent used for a variety of polymers for microelectronics, in *Midel* transformer oil and others. Importantly, no additional surface modification is required.

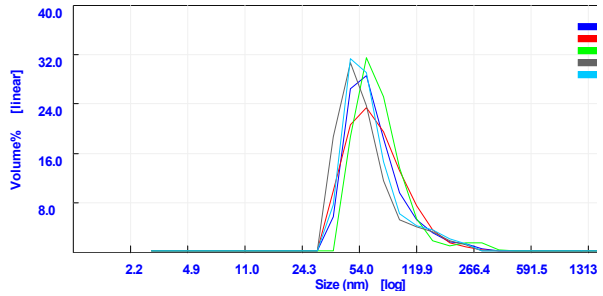

Figure 3. *Volumetric size distribution of the black fraction of Ch-Oz in 1-methyl-2pyrrolidinone, a solvent for polyimid and other polymers for microelectronic applications. Results of 5 repetitive measurements are shown.*

Currently, industrial scale ozone purification flow reactor is under construction at *New Technologies, Inc*.

CONCLUSION

The fractioning of commercially available detonation nanodiamonds plays an increasingly important role in the application of this product. Industrial-scale fractioning developed at *New Technologies, Inc* includes ultrasonic treatment of the suspensions as well as additional purification. Ultrasonic treatment in combination with centrifugation does not contaminate the fractions with any organic or inorganic additives. All six fractions have niche applications. Combined F1 and F2 are used for polishing pasts; when mixed with synthetic diamond powder (30/70 wt%) it becomes a highly effective polish for cut stones for jeweler. Fractions 3 and 4 can be used for superfinish polishing. Fraction 5 is recommended for applications in galvanic coatings. Galvanic coatings of nickel exhibited superior properties when deposited using fractions as compared to coatings deposited using the initial polydispersed powder[7,8]. The smallest fraction can be used as it is or further fractioned to smaller average particle sizes. As it was demonstrated at ITC, hundreds of milliliters to liters of suspensions with DND average size of 30nm can be obtained using laboratory scale equipment.

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