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NANODIAMONDS PARTICLE SIZE ANALYSIS WITH DIFFERENTIAL SEDIMENTATION

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Nanodiamond (ND) forms a part of the carbon nanomaterial family which, along with fullerenes and nanotubes, has attracted great interest in recent years due to its unique physical and chemical properties. Early studies of nanodiamonds took place in defense and weapons research but now can be found in a variety of fields for example in medicine and astrochemistry.

Nanodiamond is one of the few nanomaterials to be produced at commercial scales which stems from the production technologies developed in the 1960s. As its name suggests, it is synthesized by the detonation of solid explosives in an inert atmosphere. Nanodiamond crystallites are characterized by a narrow size distribution: most particles lie between 2 and 20 nm in diameter with average particle sizes of ~ 4 - 5 nm.

Particle size distribution was considered for analysis of medium dispersion and stability of nanodiamonds suspension by The CPS Disc Centrifuge. The graphs of particle size distribution are used in biology, engineering, in oils, in entering nanodiamods friction modifier and in many other branches of science.

The purpose of our paper is studying the Disc Centrifuge principle of operation, the method of differential sedimentation and determination of nanodiamond fraction particle sizes depending on the time for ultrasonic machining in cavitation condition.

Differential Centrifugal Sedimentation (CPS Disc Centrifuge Operating manual. Copyright 2007. CPS instrument, inc.), or DCS is a widely used analysis method that produces extremely high resolution size distribution of microscopic to sub-microscopic particles. The normal measurement range for the method is from about 0.01 micron to about 50 microns, though it is possible with some types of materials to extend the range to below 0.003 micron to up to 120 microns or more.

Sedimentation of particles in a fluid has long been used to characterize particle size distribution. Stokes' law (Stokes G.G. Mathematical and Physical Papers, 11) is used to determine an unknown distribution of spherical particle size by measuring the time required for the particles to settle a know distance in a fluid of known viscosity and density. Sedimentation can be either gravitational (1 g-force), or centrifugal (many g-force).

Gravitational sedimentation is normally limited to particles of relatively large size, because the rate of sedimentation for small particles is too low to give practical analysis time, and as Brownian motion of small particles becomes too large to allow effective settling. Sedimentation in a centrifuge extends the range of sedimentation analysis to much smaller particles. High g-force makes sedimentation of small particles much faster than Brownian diffusion, even for very small particles. When a centrifuge is used, Stokes' law must be modified to account for the variation in g-force with some distance from the centre of rotation.

$$D = \{(18\,\eta\,\ln(\frac{R_f}{R_0}))\,/((\rho_p - \rho_f)\omega^2\,t\}^{0.5}$$

D - the particle diameter (cm)
ρ_P - particle density (g/ml)
ρ_F - the fluid density (g/ml)
G - the gravitational acceleration (cm/sec^2)
η - the fluid viscosity (poises)

R_0 - the initial radius of rotation (cm)
ω - the rotation velocity (radians/sec),
R_f - the final radius of rotation (cm).

All of the parameters except time are constant during the analysis with a centrifuge running at constant speed and temperature. We know the values of these well or can accurately measure their. The modified form of Stokes' law accurately measures the diameter of spherical particles by their arrival time to the detector.

There are two common sedimentation methods: integral and differential.

Integral method (Figure 1) is the oldest of the sedimentation method. A detector beam (a light beam or X-ray beam) passes through the fluid at a know distance from the fluid surface and measures particle concentration. The initial intensity of light or X-ray reaching the detector is a minimum, corresponding to the maximum concentration of particles. As a particle settle through the fluid, the concentration of particles remaining in the dispersion falls and the intensity of light or X-ray that reaches the detector increases. Stokes' law is used to calculate the size of particles that sediment out of the fluid as a function of time and a particle size distribution is generated by plotting the measured concentration of particle size distribution. The method is called integral sedimentation because the sum of all particles smaller than a particular size is being continuously measured during the analysis. A differential particle size distribution can be generated from the integral results by applying mathematical differentiation with respect to diameter.

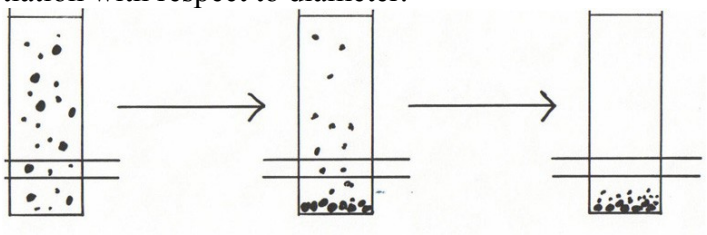

Figure 1 - Integral Sedimentation Method

Differential sedimentation (see Figure 1) was first reported in 1930 (Marshall C.E. Proc. Roy. Soc., A 126 427). A sample of particles to be analyzed is placed on top of a column of clear liquid at the start of the analysis and particles settle according Stokes' law, just as in integrals sedimentation. The detector initially reads maximum intensity indicates the concentration of particles in the detector beam. When an X-ray beam is used, the reduction in intensity is proportional to particle concentration. When a monochromatic light source is used, Mie theory light scattering can be applied to the intensity data to calculate particle concentration.

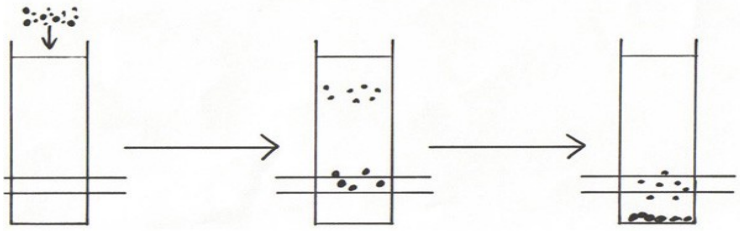

Figure 1. Integral and Differential Sedimentation Method

When all particles have passed the detector, the signal returns to the original level. A plot of the particle concentration against the calculated particle diameter produces a differential distribution. At any time during the analysis, only particles of one particular size range are being measured by the detector beam; all larger particles have already passed the beam, and all smaller particles have not yet arrived. The method is called differential sedimentation because only a tiny part of the distribution is being measured by the detector beam at any time.

The differential size distribution and its corresponding integral distribution of 3 minutes ultrasonic machining nanodiamonds are shown in Figure 3.

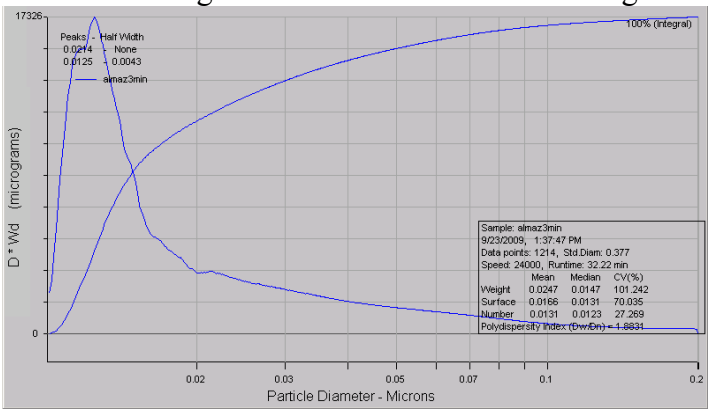

Figure 3. Differential and Integral Distribution of 3 minutes ultrasonic machining ND

DCS Instruments Design

The most common design for DCS instruments is a hollow, optical clear disc that is driven by a variable speed motor. A typical disc cross section is shown in Figure 4. The disc can be of virtually any size, but manufacturers have settled on a diameter of approximately 125 to 150 mm. The detector beam is usually monochromatic light of relatively short wavelength (400 nm – 500 nm); though some instruments use a longer wavelength light to provide better detector sensitivity when particles smaller than 100 nm are measured.

To prepare the instruments for analysis, the disc is set in monitor at constant speed, and then the disc chamber is filled with a fluid which contains a slight density gradient. Sample is prepared for analysis by dilution in a fluid of slightly lower density then least dense fluid in the disc. The lower density fluid used for the sample reduces initial mixing of the fluid inside the disc with the sample. When a sample is injected (normally using a small syringe), it strikes the back inside face of the disc, and forms a thin film, which spreads as it accelerates radially toward the surface of the fluid. When the sample dispersion reaches the fluid surface, it quickly spreads over the surface, because it is lower density. Once a sample is on the fluid surface, sedimentation of individual particles begins. The injection of a sample is rapid (<50 milliseconds), so the starting time for an analysis is well defined, and the precision of sedimentation time is quite good.

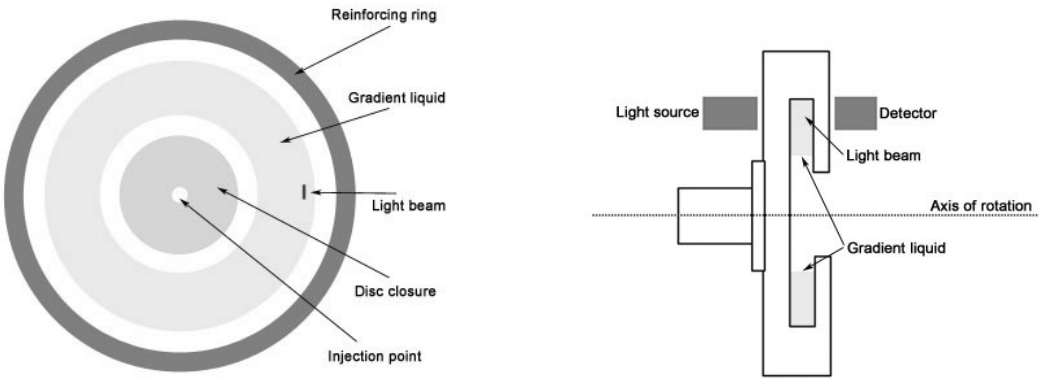

Figure 4 – Hollow Disc Centrifuge Design

When the analysis is completed, the instrument is ready for the next sample. There is no need to empty and clean the centrifuge, so many samples can be run in sequence without stopping the centrifuge. The only limitation on continuous run time is that the density gradient slowly degrades due to molecular diffusion. When the density gradient is no longer steep enough to maintain stable sedimentation, the instrument must be stopped, emptied, and a new

gradient formed. Typical gradient lifetime is 2 to 72 hours, depending on the molecular weight and viscosities of the materials that formed the gradient.

Accuracy and repeatability of the DCS method are very good in nearly all cases. Any significant inaccuracy in the results is caused by either inaccurate values for the physical parameters of the system, instability in the sedimentation, or by deviation of the sedimentation from Stokes' law. DCS gives distributions that have excellent resolution.

Progress of Experiment

The subject of investigation is nanodiamond aqueous suspension that originates from a detonation of an explosive mixture of trinitrotaluol (TNT) ($C_7H_5N_3O_6$) and RDX ($C_3H_6N_6O_6$) in gaseous and liquid media. The nanodiamonds were synthesized in CO_2 medium and were purified from non-diamond carbon by atmospheric heat treatment process with boric oxide B_2O_3.

For analysis were chosen 3 nanodiamond samples, which differed from each other by dispersion time. The first sample was not dispersed, second sample was 3 minutes, third was 6 minutes.

The graphs of distribution are shown in Figure 5 mentioned below. In these figures the differential curves are built in logarithmic scale.

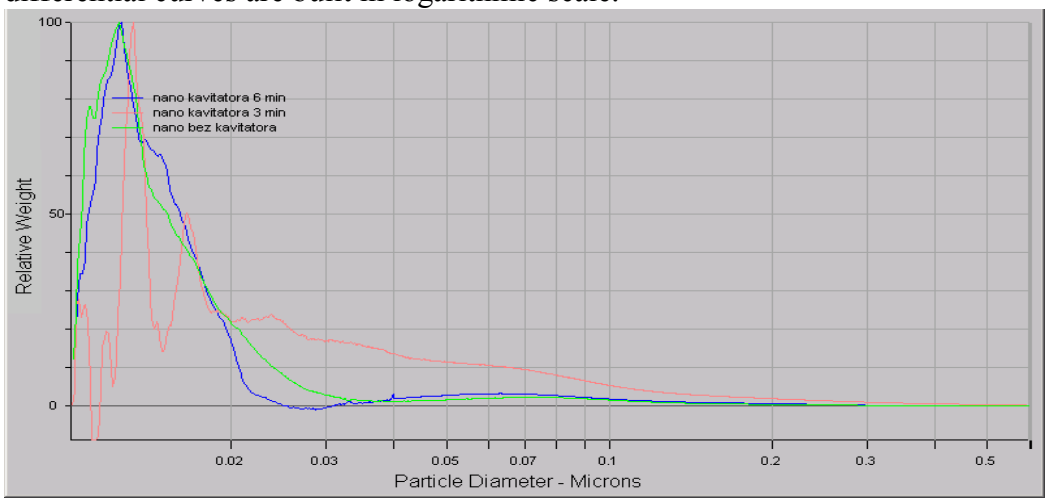

Figure 5. Graphs of distribution of particles mass concentration of a non-dispersed ND suspension (green), 3 minutes dispersion ND (red) and 6 minutes dispersion ND (blue), depending on their sizes

It is seen from graphs that the sizes of principal particles number for each investigated sample are less then 100 nanometers. When we dispersed sample, 3 minutes particles sizes increase occurred. Thus we have the aggregation process. Further dispersion time increase to 6 minutes results in the disaggregation process.

These results are comparable with literature facts about ultrasound treatment time influence on the distribution curve form of ND particles sizes.