



## Nanodiamonds of Laser Synthesis and Prospects of their Commercialization

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The Global market of Nano-Diamond (ND) powders was investigated and the main factors restricting the industrial implementation of ND with the average size of 4-5 nm have been defined: non-constant quality and surface reactivity of commercially available ND, the absence of industrial technologies for dispersing ND in solvents and polymers and insufficient number of ND formulations validated by potential ND consumers. The solution proposed for overcoming the barriers combines the fabrication of pure, uniform and low-cost ND by Light Hydro-Dynamic Pulse (LHDP) technology, industrial Production of Advanced Nano-Diamond Additives (PANDA) in forms of ready-to-use modified ND powders, ND slurries and masterbatches and validation of ND formulations by potential industrial consumers. Technological and economic feasibility of industrial implementation of LHDP was investigated and the possibility of 200-fold increase in the productivity of the synthesis and cost reduction was confirmed. The experiments with ND synthesis varying the parameters of laser irradiation were performed and the obtained ND were characterized by X-Ray diffraction and weighted. It was found, that the minimal power density in the spot needed for ND synthesis by the LHDP was  $10^6$  W/cm<sup>2</sup>; however, only less than 40 % of this powder had the diamond cubic structure, while the rest part was the amorphous carbon. The power density of  $10^7$  W/cm<sup>2</sup> provided 100 % crystallinity of ND powder not affecting the average size of 4.5 nm. Enhancing the power density from  $10^7$  to  $10^{10}$  resulted in the 2-fold output increase and not affected the average size of ND and crystalline structure. The power density close to  $10^{11}$  W/cm<sup>2</sup> led to the appearance of bigger ND particles (20-30 nm in average, ~15 %) in ND of 4-5 nm. The optimization of laser beam parameters enabled to attract a commercially available laser system for industrial fabrication of ND powder with the projected ND output of 600 g/hour.

A technological chain for PANDA consists of two independent manufacturing lines: for laser ND synthesis and for ND surface modification, disaggregation and uniform incorporation within various media. Ready-to-use ND additives have been developed in the form of modified ND powders, nano-fluids based on diverse solvents (aqua, acetone, cyclohexane, N-methyl-2-pyrrolidone, isopropyl alcohol, 2-Butoxyethanol, dimethylformamide, etc.) with high ND concentration (up to 10 wt. %) and high colloidal stability (no sediments within at least 6 months), and masterbatches based on polyester oil, wax, stearic acid and epoxy resins. PSD was analyzed. Preliminary results of testing ND additives in new applications: 3D printing, thermal management, high refractive index of polymers and energy storage, are presented. It was found that ND dispersed in water, oil and epoxy resin increase in their heat dissipation ability and the effectiveness of ND for diverse basic materials is different. The highest thermal conductivity was determined in ND compounds containing 2 fillers: ND and graphene.

Approaches for accelerating of ND uptake in traditional applications (coatings, lubricants, polishing and polymers) and scientific issues for ND characterization, validation and new applications development (for bio-medicine, thermal management and high refractive index of polymers) are discussed. A new approach of effective cancer treatment with modified ND is proposed.

Nanodiamond (ND) particles have cubic crystal lattice with unique properties of diamond in the core and hybrid graphene-like structure with functional groups on the surface. Specially designed and controlled surface chemistry of NDs enables to bond crystallites with average size of 4-5 nm with molecules of chosen materials improving their functional properties, hardness and wear resistance, thermal conductivity and electrical resistivity, optical, electronic and magnetic characteristics, as well as their bio-compatibility, manufacturability and durability. A new process for producing diamond nano-additives has been developed. Two manufacturing lines were designed: for manufacturing ND by Light Hydro-Dynamic Pulse (LHDP) technology and for Production of Advanced Nano-Diamond Additives (PANDA) by surface modification of ND, their disaggregation and uniform particles distribution within basic materials.

Final formulations of ND additives in the form of powders soluble in numerous fluids with differently functionalized surface of nanoparticles, stable concentrated ND slurries based on various solvents (aqua, acetone, cyclohexane, N-methyl-2-pyrrolidone, isopropyl alcohol, 2-Butoxyethanol, dimethylformamide, etc.) and masterbatches based on diverse polymers (polyester oil, wax, stearic acid and epoxy resins) are presented.

The performance of ND additives is demonstrated for the following selected applications:

- a) Antifriction lubricants for lapping / finishing: ND act as lapping agents, being 50 times harder than steel, ND introduce into friction surfaces and create protective diamond nano-layer, reduce friction and wear, improve the load-bearing tolerance of friction surfaces and extend the lifetime of parts and mechanisms by the factor of 1.5–4.0; ND in engine lubricants reduce the fuel consumption by 5-10 %.
- b) Metal coatings: ND additives to electrolytes improve electroplating and electroless deposition processes, resulting in high density of coatings (reducing grain size of metals and enhancing uniformity of the coating layers) and improving their performance (wear, corrosion and chemical resistance), in chromium galvanization ND increase the service life of parts and mechanisms by the factor of 2-10; in Ni-B coatings ND increase in the microhardness up to 8000 kg/mm<sup>2</sup> extending the surface life by the factor of 6; in gold and silver electroplating ND additives enable to reduce the consumption of precious metals by the factor of 2-3 (since these coatings at the thickness of 0.1-0.3 μm are of high density, homogeneous and defect-free).
- c) Fine polishing: ND additives to polishing slurries and pastes enable to reduce the roughness of polished surfaces up to 0.5 nm and to accelerate the process of finish polishing of optic crystals, wafers and diamond CVD films.
- d) Polymers: in general ND additives increase in the wear, radiation, corrosion, frost and aging resistance of polymers, in their heat conductivity and electrical resistivity; in ABS filaments for 3D printing, ND enhanced the productivity of extrusion by minimum 50 %, increased in the stiffness and elastic modulus by 22.5 %, the tensile strength and load of break enhanced by 14.5 %, the prolongation at break was reduced by 94 %.

Novel ND applications, such as catalysts for numerous chemical processes, EMI shielding, polymers with high refractive index, thermal conductive insulation materials and wide range of other functional materials with improved properties, are presented.