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Nanodiamond graphitization and properties of onion-like carbon.

Nanodiamond (**ND**) reactivity and graphitization ability limit the temperature range where ND can be effectively used. At the same time new nanocarbons (**NC**) can be produced using controlled ND graphitization (namely: onion-like carbon (**OLC**), sp^2/sp^3 nanocomposites). Here we present the comparative study data on the diamond graphitization with a special effort on low temperature graphitization (1370-1870 K).
Diamond graphitization was studied on a wide set of diamond and diamond containing samples (high explosive's detonation soot, ND, micron size diamond, CVD, diamond films and diamond single crystals). The graphitization products were characterized using HRTEM, XPS, XRD, Raman spectroscopy and other techniques. It was found that OLC is formed during the annealing of nanodiamond while the annealing of micron size diamond produces closed curved graphite-like structures (nanotubes, nanofolds etc.). ND graphitization in explosion conditions can be accompanied by gas transfer reactions leading to the formation of ribbon-like graphitic particles.
Theoretical consideration based on molecular modeling using combination of molecular mechanics, molecular dynamics and HF methods allows to propose that the formation of OLC and closed curved graphite species on a diamond surface have features of self-assembling processes. The bulk density of graphitized nanodiamond was measured by a gamma-ray attenuation method. These data combined with small angle x-ray scattering (SAXS) and true density measurements of the samples heated at various fixed temperatures were used to study the graphitization kinetics of diamond. Comparison of that kinetic data with the 'classical' data of Evans and Davies for the high temperature region (>2000K) leads us to conclude that there are at least two temperature regions in which the diamond graphitization occurs by different mechanisms. The Debye temperature for diamond, 1910 K, appears to serve as the boundary between these regions. At and above this temperature all oscillating freedom degrees are excited and the graphitization involves the displacements of individual atoms. In the low temperature regime, the graphitization starts on surface defects and proceeds via a 'concert' mechanism where the energy required for breaking the C-C bonds is simultaneously compensated by the formation of new bonds. The diamond–graphite interfaces which we observe to involve the transformation of three diamond (111) planes into two graphite (0002) planes, illustrates this mechanism.
The knowledge of the kinetics of ND graphitization provides us with the possibility to produce the diamond/nanographite composites with variable ratio of decreasing in size diamond core and defective curved graphitic shells (sp^2/sp^3 nanocomposites). Small size of curved graphitic shells, the presence of interface between nanosize diamond cores and graphitic shells and probably high concentration of open graphitic edges can cause the unusual electronic properties of these composites and OLC. All these materials are under intensive studies. They were characterized with HRTEM, Raman spectroscopy, XRD, XPS, EELS, ESR, X-ray emission spectroscopy and the electrical resistivity measurements. Potential applications of new nanocarbons will be shortly considered.