
METHODS OF FABRICATION AND PROCESSING OF DETONATION NANODIAMONDS

Selective Inhibition of the Oxidation of Nanodiamonds for Their Cleaning

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Abstract—The effect of selective inhibition of nanodiamond oxidation upon heating of detonation carbon in air is used to extract nanodiamonds from the detonation products. The methods for cleaning nanodiamonds from nondiamond carbon modifications are described depending on the synthesis conditions. © 2004 MAIK “Nauka/Interperiodica”.

One of the most important problems in cleaning synthetic diamonds is to remove them from carbon that did not transform into the diamond phase. In the chemical methods of cleaning, conditions are chosen under which nondiamond carbon (graphite or soot) is more reactive. Different reaction rates, e.g., oxidation rates, are explained by the different reaction mechanisms (formation of layered graphite compounds), by the effect of graphite porosity or of the large surface of soot, and by the significantly different oxidation activation energies (including oxidation in glow-discharge plasmas). The carbon that condenses upon the detonation of explosives is extremely dispersed and possesses an imperfect structure; therefore, it is highly improbable that the mechanisms of oxidation of different modifications of detonation carbon differ radically. The specific oxidation behavior of detonation carbon was confirmed in experiments on the oxidation of the products of detonation of a trinitrotoluene–hexogen mixture in an air glow-discharge plasma.

Glow discharge was initiated in a quartz tube 50 mm in diameter and 600 mm long. The interelectrode distance was varied from 200 to 400 mm, and the discharge current, from 0.1 to 2 A. The device was placed in a volume pumped out to 10^{-2} mmHg. A system of inlet valves and differential pressure gages allowed us to maintain a controlled atmosphere of various gases in the range 1–100 mmHg. To remove the diffusion restrictions, samples to be studied were arranged as a thin layer on the bottom of a flat alundum crucible in the zone of the positive column of the glow discharge. The oxidation products were examined by using x-ray diffraction, standard techniques of chemical analysis, and back chromatometric titration.

The kinetic-oxidation data for the detonation carbon and the oxidation products show that the majority of nondiamond carbon (more than 60% of its total content under the experimental conditions) oxidizes at a high rate. The rest of the carbon oxidizes at a rate that is

close to the oxidation rate of diamonds. The imperfection of the nondiamond carbon, of course, has an effect on the different oxidation rates, but it cannot completely explain this nonuniform reactivity. The oxidation rate of diamonds increases with the content of metallic impurities in the initial powders (originating from the explosion chamber and detonator), which indicates the necessity of taking their catalytic influence into account.

To study the kinetics of the isothermal oxidation of various detonation-carbon modifications by atmospheric oxygen, we took nanodiamonds (extracted from the detonation products by boiling in a mixture of sulphuric and nitric acids) and nondiamond carbon synthesized under conditions unfavorable for the formation of the diamond phase. To remove metallic impurities, the powders were boiled in dilute acids. After having been washed in water and dried, the powders had almost equal specific surfaces (about 270 m²/g) and contents of metal-containing impurities (less than 0.5%). Upon heat treatment in air, the diffusion restrictions were absent, which was indicated by the relative powder mass loss being independent of the sample weight. The experiments showed that, up to a certain degree of transformation ($\alpha \leq 0.3$), the oxidation of all samples proceeded as in a reaction in which all particles retain their shape; as a result, we could use the Roginskii–Schulz equation to calculate the reaction rate. The diamond powder mass loss after the time τ of isothermal oxidation is given by [1]

$$(m/m_0)^{1/3} = 1 - A\sigma_0\tau\exp(-E/RT)/3,$$

where m_0 is the initial powder mass, m is the powder mass at the instant of time τ , A is a constant, σ_0 is the initial specific surface of the powder, and E is the oxidation activation energy [1].

Using the temperature dependences of the reaction rates, we calculated the oxidation activation energy for nanodiamonds (about 180 kJ/mol) and the average oxi-

dition activation energy for nondiamond carbon (~160 kJ/mol). These results explain why it is difficult to retain diamonds during the gasification of nondiamond carbon by heat treatment in air. Catalysts are traditionally applied to selectively oxidize untransformed carbon for cleaning synthetic diamonds. The relatively low oxidation temperatures of detonation carbon allow us to apply another method, namely, selective inhibition of diamond oxidation. A study of the effect of boron-containing compounds on the oxidation of detonation carbon showed that the oxidation rate decreases significantly. When using boric anhydride, we chose conditions for which diamonds were completely retained with a residual nondiamond carbon content of less than a fraction of a percent. To reveal the mechanism of the effect of the boron-containing compounds, we studied the kinetics of oxidation of nanodiamonds and nondiamond carbon in the presence of boric anhydride at various temperatures. The results show that the activation energy of oxidation remains almost unchanged for nondiamond carbon and increases substantially for diamonds (to 250 kJ/mol). The selectivity of oxidation inhibition makes it possible to separate the diamond and nondiamond modifications of detonation carbon. This finding was applied to develop a method for cleaning nanodiamonds [2]. The optimum cleaning conditions, including the temperature and the amount of boric anhydride, depend on the characteristics of the detonation carbon, such as the ratio of the quantities of the diamond and nondiamond modifications and the fraction of more ordered graphite-like carbon. The table gives the conditions for removing nondiamond carbon that make it possible to retain the maximum amount of nanodiamonds depending on various parameters of their synthesis.

The extraction of nanodiamonds by using this method of removing nondiamond carbon was performed at the pilot bay of the Department of the Physics of Nanophase Materials (Krasnoyarsk Scientific Center) and of the Krasnoyarsk State Technical University. The products made at the pilot bay are certified. Nanodiamonds produced using this method and diamonds produced by other manufacturers were compared by us and other researchers. Chiganova *et al.* [3] showed that, as compared to diamonds from acid cleaning, the oxidation rate of the nanodiamonds thus produced is significantly lower and the sedimentation stability of sus-

Techniques of cleaning nanodiamonds depending on the synthesis conditions

Charge composition	Conservation medium	Average temperature, K	Treatment time, h
Trinitrotoluene/hexogen	CO ₂	770	2.5
40/60	N ₂	740	3.0
Trinitrotoluene/hexogen	CO ₂	770	3.0
60/40	H ₂ O	800	3.0
	Ice (shell)	820	2.0
Graphite	N ₂	920	4.0

pensions fabricated through ultrasonic dispersion of powders in water is higher. Our technology provides the minimum size of particle aggregates among the powders studied in [4]. According to [5, 6], our technology provides a significant output of individual diamond particles about 4 nm in size, which was used to produce two-dimensional diamond crystals.

Thus, the surface modification of nanodiamonds upon cleaning by the method proposed in [2] can be useful in a number of technical applications of nanodiamonds.

REFERENCES

1. O. N. Breusov, V. M. Volkov, V. N. Drobyshev, and V. F. Tatsii, *Interaction of Diamonds to Liquid and Gas Media* (Naukova Dumka, Kiev, 1984), p. 23.
2. RF Patent No. 2,004,491, Byull. Izobret., Nos. 45–46, 85 (1993).
3. G. A. Chiganova, A. S. Chiganov, and Yu. V. Tushko, *Neorg. Mater.* **30** (1), 56 (1994).
4. A. Ya. Korets, E. V. Mironov, V. P. Malyi, and E. A. Petrov, in *Proceedings of II Interregional Conference on Ultrafine-Dispersed Powders, Nanostructures, and Materials* (Krasnoyarsk, 1999).
5. S. V. Kukhtetskii and L. P. Mikhaïlenko, *Kolloidn. Zh.* **58** (1), 137 (1996).
6. S. V. Kukhtetskii and L. P. Mikhaïlenko, *Dokl. Akad. Nauk* **357** (5), 616 (1997) [*Phys.–Dokl.* **42**, 661 (1997)].

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