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Solid State Phase Transition of Nanodiamond upon Heating and Irradiation

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Abstract

The data on the destruction of a diamond single crystal and detonation nanodiamond (**DND**) under radiation exposure are analyzed. The irradiation dose at which graphitization occurs in a single crystal of a diamond is determined. The influence of the DND particle size on the nature of damage during irradiation has been established.

An experimental study of the thermal stability of DNDs at atmospheric pressure in a dynamic argon medium in the temperature range from 30 to 1500 °C with a heat treatment rate of 2 and 10 °C/min is carried out. A same part of DND demonstrates high stability above 1500 °C. A investigation with using X-ray diffraction analysis showed that the solid-state phase transition to DND occurs at about 1000 °C. The examination of the stored samples on an electron microscope showed the influence of the heating rate on the parameters of the DND powder. The data on thermal stability were recommended to improve the technique of ion-plasma coating on the surface of steel parts.

Keywords

Detonation nanodiamonds; synchronous thermal analysis; thermal stability; solid state phase transition; radiation damage.

Introduction

The internal structure of nanoparticles differs from the structure of a bulk crystalline substance [1]. This is due to the large influence of the nanoparticle surface on the crystal lattice. Atoms in the surface layer have neighbors only on one side, this leads to a change in the equilibrium and symmetry of forces and masses, causing a change in the interatomic distances. The change in lattice parameters affects the properties of the entire substance as a whole. Thus, for example, the temperature of the graphitization beginning of bulk diamond at atmospheric pressure exceeds 1500 °C, and the beginning of nanodiamond particle graphitization occurs at temperatures below 1000 °C [2]. Due to its small size, the nanomaterial may have properties that are not possible in a bulk state. This circumstance expands the area of application of nanoparticles in various spheres of human activity.

To date, most of the diamond nanoparticles are produced by detonating high explosives. However, the wide use of this material is limited by the ambiguity and contradictoriness of its properties, available the literature data. This is due to the inhomogeneous structure of detonation nanodiamond particles. The particle has a diamond core and an impurity shell, which consists of non-diamond carbon, metallic impurities, and the radical groups C–H, C–N, C–O located on the surface.

Investigation of the nanodiamond particle stability under various external impacts will give a better understanding of the diamond powder behavior and expand its applicability.

The purpose of this paper is to analyze the data on the solid phase transition in nanodiamond under exposed to irradiation, and to study of the effect of the thermal processing.

Radiation stability of diamond

Irradiation of a diamond single crystal has shown that the irradiation dose might cause point defects, an amorphous path in the material, and a graphite phase can appear in the ion track [3]. Thus, when diamond was irradiated with silicon ions with an energy of 1 MeV, a dose of 1×10^{15} Si^{+}/cm^{2} at room temperature,

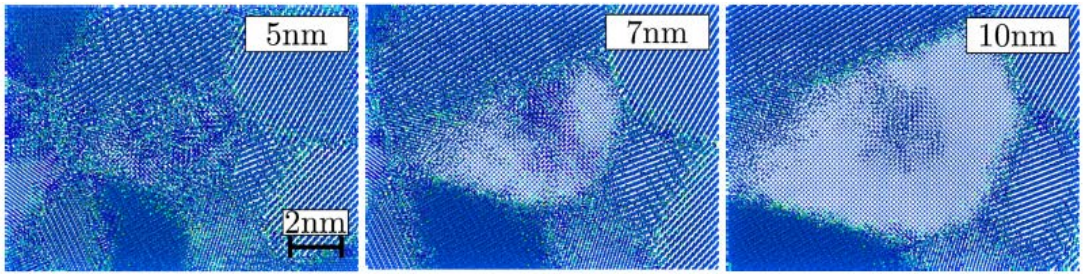


Fig. 1. Molecular dynamics simulation of irradiation of nanodiamond particles by heavy fast ions with an effective stopping energy of 17 keV/nm depending on the particle size [5]

point defects were observed in the sample. Annealing the irradiated sample at a temperature of 1350 °C for 24 hours resulted in the restoration of the defects to an ideal diamond lattice.

Annealing of an irradiated sample of a detonation nanodiamond by fast neutrons led to the release of Wigner energy in the temperature range from 230 to 450 °C. And with an increase in the exposure time of the neutron beam to the sample, the amount of energy released during subsequent annealing in an inert atmosphere increased [4].

When irradiated with silicon ion with the energy of 1 MeV, a dose of 7×10^{15} Si^+/cm^2, an amorphous carbon was formed in the ion track [3]. When the irradiated sample was annealed at a temperature of 1350 °C for 24 hours, graphite was formed from the amorphous phase.

The influence of grain size of nanodiamond on the character of damage during irradiation with fast heavy ions was shown in [5]. When irradiated with heavy ions with effective stopping energy of 17 keV/nm, particles with a size of 5 nm completely became amorphous. After irradiation, particles of 7 nm in size had an amorphous phase surrounded by a diamond. In a particle measuring 10 nm, only a few point defects were observed (Fig. 1).

Thus, the analysis of literature data on the radiation impact on the diamond phase showed that the nanodiamond material is a good sensor in the targets to identify processes occurring in samples exposed to radiation. The content of the saved diamond phase appears to be a function of the type and dose of irradiation.

The conditions of structural-phase transformations depend on the type of action on the substance. It has been experimentally established that irradiation can significantly change the conditions of phase transformations, induce new phases, which affects the performance characteristics and applicability of the material. Before the experimental study of the radiation stability of detonation nanodiamond the theoretical analysis was made of the thermal stability of this material.

Thermal stability of nanodiamond

In this work, the behavior of detonation nanodiamond was analyzed with increasing temperature. Heat treatment was carried out by the method of synchronous thermal analysis in the range from room temperature to 1500 °C with the rates of 2 and 10 °C/min in a dynamic atmosphere of argon.

The initial data of the nanodiamond obtained by the explosion of a mixture of TNT/hexogen (50/50) were given in [6]. After the heat treatment, the stored samples were investigated by X-ray phase analysis and electron microscopy.

The heating the DND sample to 1500 °C at a rate of 10 °C/min resulted in the mass loss was about 16 %. With an increase in the temperature, the radical groups and adsorbed water were removed from the surface of the particles. This process led to a decrease in the mass of the sample by 10–20 % [7].

The X-ray diffraction analysis of the stored samples before and after heat treatment is shown in Fig. 2. From the ratio of the integrated intensities of the base plane of diamond (111) at 2θ = 44° on the X-ray line it was found that the diamond phase decreased with increasing processing temperature (Fig. 2, lines *2 – 5*).

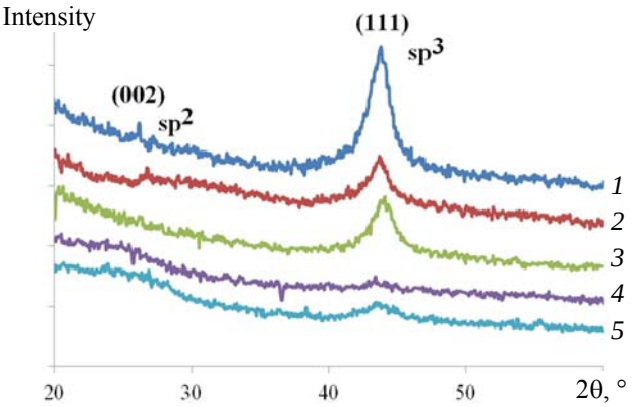
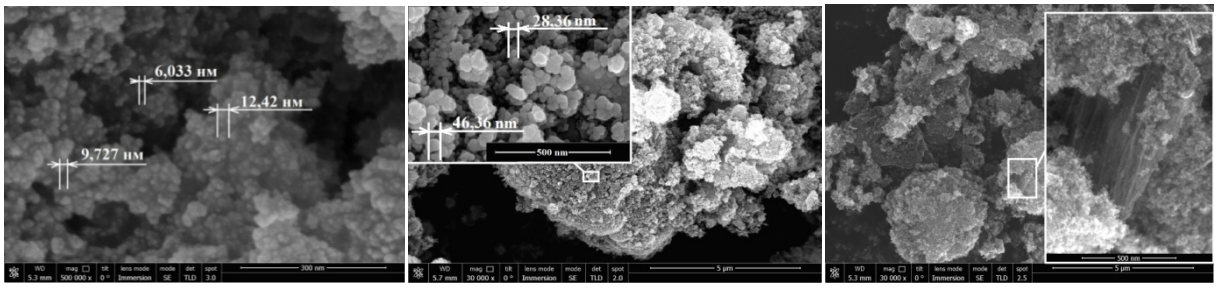


Fig. 2. Diffractograms of DND samples before and after heat treatment:
1 – initial sample; *2* – heated to 600 °C with *v* = 10 °C/min; *3* – heated to 1000 °C with *v* = 10 °C/min; *4* – heated to 1500 °C with *v* = 10°C/min; *5* – heated to 1500 °C with *v* = 2 °C/min (*v* is the rate of heat treatment)



a) *b*) *c*)

Fig. 3. Microstructure of nanodiamond powder:
a – initial sample; *b* – after heat treatment up to 1500 °C at *v* = 10 °C/min; *c* – heated up to 1500 °C at *v* = 2 °C/min

As can be seen from Fig. 2, the graphite peak on the X-ray line from the base plane (002) 2θ = 26° did not increase with increasing temperature. This might mean that the original DND particles underwent destruction, as a result of which they did not go into a crystalline ordered graphite structure with sp^2-bonds, but into an amorphous state, the amount of which cannot be determined by the X-ray method. However, at 1500 °C a halo appeared in the region of Bragg angles 2θ = (20–32)°, which corresponded to a graphite-like X-ray amorphous phase (Fig. 2, lines *4*, *5*). As in the case with graphite, it was a carbon structure consisting of sp^2-bonds in the plane, but the interplanar distance (0.3707 nm) turned out to be larger than that in graphite. Such a structure was stable and, upon further heating, did not go over into ordered graphite. In addition to the X-ray amorphous graphite-like structure, the crystal structure of the diamond was observed in the sample heated to 1500 °C in an amount of 10% of its content (Fig. 2, lines *4*, *5*).

The study of microphotographs of nanodiamond samples before and after heat treatment are shown the influence of the heating rate on the parameters of the powder particles [3].

The initial material of the nanodiamond powder consisted of nanoparticles with sizes of 6–8 nm (Fig. 3*a*). After heating the nanodiamond sample at a heating rate of 10 °C/min to a temperature of 1500 °C, the particles were spherically shaped with sizes of 30–40 nm (Fig. 3*b*) [8]. The characteristic particle size of the powder increased with an increase in the temperature. Perhaps, the individual nanoparticles were "sintered" together. As a result, sintered conglomerates were formed, which can be observed in Fig. 3*b*. When heated at a rate of 2 °C/min, the size of the spherical particles was less than 10 nm and planar formations appeared (Fig. 3*c*), the nature and origin of which requires further investigation.

The data obtained for the thermal stability of nanodiamond particles can be useful for developing new composite materials on their basis and optimizing the process of ion-plasma hardening of the surfaces of steel parts.

The solid phase transition of sp^3 to sp^2 causes a change in the diffraction pattern, which makes this transition promising for diagnosis. The combination of diamond structure and nanosizes and porosity [9] makes it easier to emit radiation from the diagnosed volume. In combination with the studied thermophysical transition conditions, this can be used to diagnose Warm Dense Matter.

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