

Thermal conductivity of sintered nanodiamonds and microdiamonds

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Abstract

We studied the sintering mechanisms and thermal conductivity of composites based on well purified detonation nanodiamonds (ND) prepared by Dr. Aleksenskii A.E. The thermal and electrical conductivities of composites from natural diamonds of 10–14 μm in size were also examined. Both types of composites were sintered at high pressures (5.0–7.0 GPa) and high temperatures (1200–2300 $^{\circ}\text{C}$) for 10–25 s. It was found that the thermal conductivity of composites from natural diamonds increased as the sintering temperature approached the diamond–graphite equilibrium in the pressure range of 4.5–6.5 GPa because of the interdiffusion of the diamond particles. Above the phase equilibrium temperature, the thermal conductivity was observed to decrease due to the sample bulk graphitization.

The maximum value of this parameter for the ND samples was observed at approximately 1900 $^{\circ}\text{C}$. Higher temperatures caused sample damage at lowered pressures, which seems to be due to the ND transition to the nondiamond carbon phase possessing a lower density. When we added 5 wt.% of C_{60} fullerene to the initial ND, the diamond transition to a nondiamond carbon-like state occurred at a temperature below 1400 $^{\circ}\text{C}$ and the thermal conductivity increased from 50 to 100 $\text{W}/(\text{m}\cdot\text{K})$.

Thermal conductivity was found to be about 50 $\text{W}/(\text{m}\cdot\text{K})$ for the ND samples and about 500 $\text{W}/(\text{m}\cdot\text{K})$ for the microdiamonds.

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1. Introduction

The thermal conductivity of diamonds with copper produced of 1420–1470 K and at 4.5 GPa for 15 min may be very high but seldom exceeds 600 $\text{W}/(\text{m}\cdot\text{K})$ at room temperature, varying with the diamond crystallites comprising the composites [1]. The sintering of a diamond–cobalt system [2] has shown that this process involves surface graphitization of the initial diamond in the range of its thermodynamic stability at 5.8 GPa and at temperatures of 1300, 1400 and 1500 $^{\circ}\text{C}$. During sintering, cobalt interacts with graphite formed on the diamond crystallites, followed by the graphite transformation to diamond. Direct bonding between diamond grains is very difficult to achieve when a pure diamond powder is sintered without a metallic catalyst, even at temperatures as high as 2000 $^{\circ}\text{C}$ and at a pressure of 7.7 GPa for 1 h [3]. Hall [4] reported the density of a sintered composite to be 3480 kg/m^3 (99% of the relative density) when sintering was performed at

8.5 GPa and 2170 $^{\circ}\text{C}$ for 3 min. Stromberg and Stephens observed diamond sintering at 6.0–6.5 GPa and 1800–1900 $^{\circ}\text{C}$ [5]. The authors of [6] found that the thermal conductivity of diamond polycrystals was 543 $\text{W}/(\text{m}\cdot\text{K})$ at 20 $^{\circ}\text{C}$. When a diamond powder consisting of grains smaller than 0.5 μm was sintered at 5.8 GPa and temperatures of 1370 and 1400 $^{\circ}\text{C}$ for 30 min, the samples represented weakly bonded structures because their grinding resistance was very low [7]. The authors concluded that the sintering temperature was too low for direct bonding to occur between the diamond grains. In another experiment, a diamond powder with a grain size ranging from 3 to 5 μm was sintered in a toroidal chamber at pressures of 8–9 GPa and temperatures of 1700–2400 $^{\circ}\text{C}$ for 60 s [8]. When diamond was sintered under different conditions without admixtures, the presence of graphite in the samples was supported by XRD data [8–10]. In these experiments, the optimal parameters of the composites, such as maximum hardness, durability, sound velocity, and density seemed to be achieved at the diamond–graphite equilibrium or at the moment of graphite formation on the diamond surface if carbide metals were preliminarily added to the initial diamond powder.

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However, little is known about the sintering of ND and their thermal conductivity. It has been found that graphitization starts at about 900 °C when nanodiamonds are annealed in vacuum. At temperatures of 1130–1630 °C, they are transformed to particles with a diamond core covered by a continuous graphite shell changing to an onion-like carbon shell [11,12]. On the other hand, nanodiamonds annealed in an argon flow at 1600 °C are transformed to nanographite [13]. It was shown in [14], however, that even a small admixture of water, carbon oxide or oxygen leads to their interaction with carbon, which results in erosion of the ND particles to produce large graphite structures with a relatively low surface energy. These workers also found that the specific surface area of onion-like carbon was nearly 1.5 times larger than that of pristine ND. The authors of [15] reported the temperature range of 1530–1730 °C, in which the graphitization rate changed. They suggest that there are two graphitization mechanisms and that the Debye temperature for diamond (1577 °C) is the boundary between the two regions. In the work of [16], ND sintering was carried out at 1400 °C and 4.5–7 GPa for 3 min. After grinding and treatment with a solution of sulfuric and chromium acids, the compact did not show the presence of onion carbon or graphite but only granules of a larger average size than that of the initial ND grains. The sintering experiments described in [17] were performed at the pressure of 8 GPa and temperatures of 1700–1800 °C for 60 s. The sample had a low Young module of about 180 GPa and was shown by X-ray diffraction to consist of diamond and graphite. To our knowledge, there is only one report [18] of ND graphitization occurring at temperatures above 1800 °C and a pressure of 7 GPa.

In the present work we studied the sintering mechanisms and thermal conductivity of ND produced by detonation synthesis. In addition, experiments were conducted on the thermal and electrical conductivities of composites sintered from natural diamonds with a grain size of 10–14 μm.

This work is another step in a series of studies on the thermal conductivity of composites based on micron-size diamonds and ND [19].

2. Experimental techniques

The initial materials were 10–14 μm natural diamonds, purified nanodiamonds and C₆₀ fullerenes of 99.5% purity. The high pressure chamber used was of toroidal type with a 6 mm inner diameter. The diameter of the composites varied from 3 to 4 mm, and their height was about 4–5 mm. Graphite bushes were used for electrical heating of the samples under pressure.

The sintering was carried out in a stabilized electrical power mode. The chamber temperature was determined from the calibration curve relating the electrical power supplied to the high pressure chamber and the temperature measured by a thermocouple. The temperature reproducibility during the heating was about 70 °C. Also, we used a high pressure calibration curve defined by the phase transitions in Bi, Ba, Tl and PbSe, PbTe.

The thermal conductivity measurements were made using a steady state technique in the temperature range of 30–200 °C in

vacuum. The temperature gradient was measured on the sample surfaces by two thermocouples. The heat flux magnitude was defined by a reference copper sample pasted in series with the experimental samples. The accuracy of the thermal conductivity measurements was about 15%.

The electrical conductivity was measured using four probes with pressure contacts. Prior to the measurement, the samples were treated in a solution of sulfuric (50%) and chromium (50%) acids and in de-ionized water to remove the residual heater graphite.

3. Results and discussion

3.1. Natural microdiamonds

The initial material for sintering was a natural diamond powder with a grain size of 10–14 μm. Fig. 1 shows the thermal conductivity data for samples produced at different temperatures and pressures varying from 5.0 to 7.0 GPa. The sintering time of natural diamonds is 11 s. One can see that increasing the pressure requires higher temperatures to be used in order to obtain a maximum of the thermal conductivity of the compact. In the pressure and temperature ranges of interest, the sintering process started at 1200 °C. The thermal conductivity of these diamonds increased as the sintering temperature approached the diamond–graphite equilibrium conditions in the pressure range of 5.0–7.0 GPa. We believe that this is due to the interdiffusion of the microdiamonds.

At the same time the surface graphitization of microdiamonds appears. This is supported by the electrical conductivity data on the microdiamond samples. Fig. 2 presents the specific electrical resistivity at room temperature of the samples sintered at temperatures 1200–2200 °C and at the pressure of 7.0 GPa. The surface of the samples produced at 7.0 GPa was purified to remove the heater graphite, followed by the measurement of their electrical conductivity. The samples with thermal conductivities less than ~150 W/(m·K) (at temperatures below

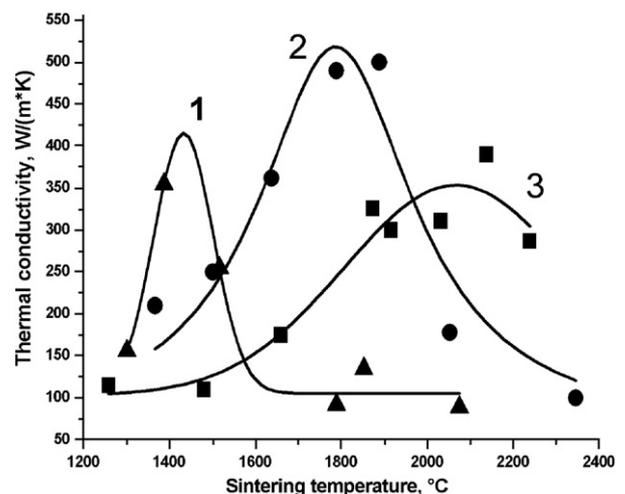


Fig. 1. Thermal conductivity of microdiamond samples produced at different sintering temperatures and pressures: 1–5.0 GPa, 2–6.0 GPa, 3–7.0 GPa.

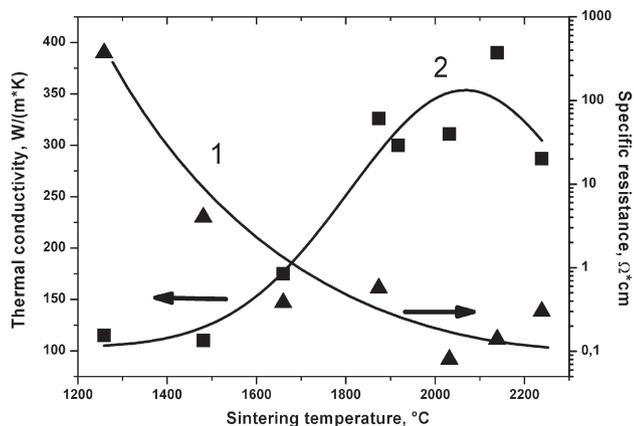


Fig. 2. Specific electrical resistivity at room temperature (1) and thermal conductivities (2) of the microdiamond samples sintered at temperatures 1200–2200 °C and at the pressure of 7.0 GPa.

1500 °C) had a milky white color, whereas the samples with thermal conductivities above 150 W/(m·K) were grey black. It is seen that the resistivity decreases starting at 1500 °C, which is likely to indicate the onset of surface graphitization and the appearance of conductivity channels associated with the graphite. The resistivity of these samples drops to 0.1 Ω·cm. Thermal conductivity rises to a considerable degree and electrical conductivity drops to a three order of magnitude with increasing of sintering temperature. Small amount of sp^2 (graphite) phase significantly change electrical conductivity because of the surface graphitization of each micron-size particle.

When the black samples were ground from the surface towards the bulk, the color and the resistivity did not change, indicating the internal homogeneity of the samples.

It is seen from Fig. 1 that the thermal conductivity rises to 500 W/(m·K) for the microdiamonds. At temperatures close to that of the graphite–diamond equilibrium, we observe a decrease in the thermal conductivity because of the bulk graphitization. This conclusion is supported by the fact that the sample volume increased by 40%, corresponding to the density ratio of graphite and diamond, and that the grinding resistance became lower. Bulk graphitization is a very rapid process at temperatures higher than that of diamond–graphite phase diagram equilibrium line. Therefore, we cannot produce samples with wide range of graphite/diamond ratio. Two samples produced at temperatures higher than that of diamond–graphite phase diagram equilibrium line (see Fig. 1 curve 1 at 1500 °C and curve 2 at 2070 °C) have diamond/graphite mass ratio ~ 0.44 . All other samples sintered at these conditions were practically 100% graphitized and those thermal conductivity was about 100 W/(m·K).

There is no correlation between density and thermal conductivity for natural microcrystalline diamond samples [19]. The density of the samples produced at temperatures lower than that of the maximum thermal conductivity is practically independent of the sintering temperature and is found to be 93–97% of the density of single crystal diamond (3.52 g/cm³). The density of samples produced at temperatures above that of the maximum thermal conductivity drops to graphite density.

It is worth noting that the maximum thermal conductivity of 500 W/(m·K) is achieved only at about 1800 °C and the respective pressure of 6.0 GPa. This is likely to be due to the optimal proportion of the microdiamonds interdiffusion and its bulk graphitization affecting noticeably the thermal conductivity.

We can conclude from these experimental findings that the increase in the thermal conductivity of samples produced by microdiamond sintering at pressures and temperatures close to those of the diamond–graphite equilibrium results from the interdiffusion of the diamond crystallites. As the temperature rises, there is a transition from the surface to bulk graphitization, so that the thermal conductivity and the density of the composite become lower.

3.2. Nanodiamonds

Fig. 3 presents our data on the thermal conductivity of pure ND sintered at 5.5 and 6.0 GPa at different temperatures. The sintering of 6.0 GPa (Fig. 3, curve 1) is seen to lead to an essential thermal conductivity rise in a narrow temperature range close to 1900 °C. It is interesting to note that heating to a temperature above 1900 °C damages the sample such that some of the material is ejected out of the chamber. This is an evidence for a considerable increase in the sample volume.

When the sintering time is increased from 11 to 25 s with a simultaneous pressure drop to 5.5 GPa (Fig. 3, curve 2), we observe a remarkable rise of the thermal conductivity and a wider temperature range in which it greatly exceeds 10 W/(m·K). Under these conditions, the achievable conductivity values may be higher than 50 W/(m·K) with the ND totally preserved. ND samples color is always grey and it does not depend on sintering temperature and density because its surface is always sp^2 .

We have shown earlier [20] that graphite with a fullerene admixture (0.3 wt.%) and a metallic catalyst stimulates the graphite–diamond transition when the sintering is performed at high static pressure and temperature. We have shown in [19] that an addition of 1% fullerenes to a microdiamond powder did

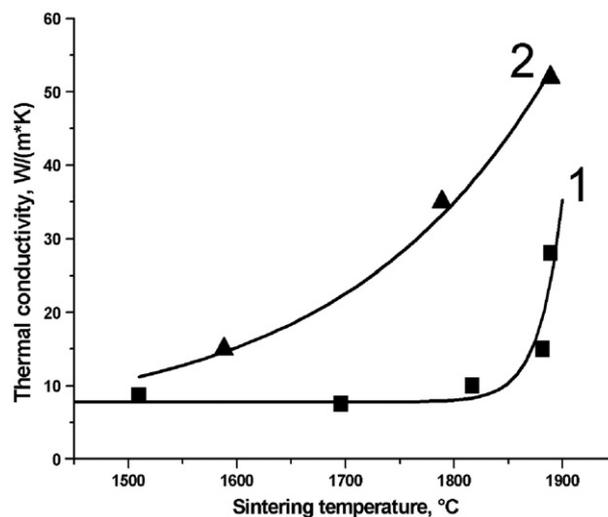


Fig. 3. Thermal conductivity of pure ND sintered at different temperatures. 1–6.0 GPa, 11 s; 2–5.5 GPa, 25 s.

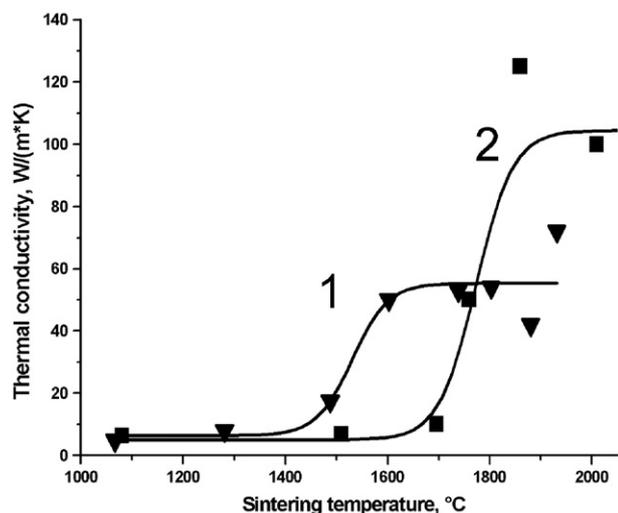


Fig. 4. Thermal conductivity of pure ND with C_{60} fullerenes (5 wt.%) sintered at different temperatures. 1–5.5 GPa, 25 s; 2–6.0 GPa, 25 s.

not practically affect the sintering parameters or the thermal conductivity of the samples.

In this work we added C_{60} fullerenes (5 wt.%) to pure ND and observed an essential change in the temperature dependence of thermal conductivity, as compared with pure ND. Fig. 4 (curve 1) shows that the thermal conductivity begins to rise even at 1500 °C of 5.5 GPa. The samples produced at a temperature above 1600 °C exhibited a considerable bulk graphitization, which was manifested as an increase in the sample volume, as compared with pure ND, and as a low grinding resistance. Their thermal conductivity was found to be close to 50 W/(m·K).

At the sintering pressure of 6.0 GPa (curve 2 in Fig. 4), the graphitization onset shifts towards higher temperatures at about 1800 °C, with the maximum thermal conductivity being ~110 W/(m·K), a value comparable with that of graphite ~100 W/(m·K).

One can conclude from this discussion that the sintered composites consist of ND and graphite (nanographite) in different proportions in the temperature range of 1200–1900 °C. Therefore, a fullerene admixture essentially affects the phase transition of nanodiamonds.

4. Conclusions

Thermal conductivity was found to be about 50 W/(m·K) for the ND samples and about 500 W/(m·K) for the microdiamonds.

The thermal conductivity of composites sintered from natural microdiamonds increases due to interdiffusion of the crystallites. The temperature range for producing composites with a high thermal conductivity becomes wider with increasing pressure. In fact, the pressure rise leads to a lower surface graphitization rate for microdiamonds. Their bulk graphitization

begins at pressures and temperatures close to those of the diamond–graphite equilibrium. As the temperature rises, there is a transition from the surface to bulk graphitization, so that the thermal conductivity and the density of the composite become lower.

Graphitization of pure nanodiamonds occurs in a narrow temperature range close to 1900 °C. Above this value, some of the material is ejected out of the high pressure chamber, indicating a considerable increase in the sample volume because of the graphitization. The fullerene admixture essentially affects the phase transition of nanodiamonds.

Thus, we suggest a sintering model which accounts for the dynamics of thermal conductivity of micro- and nanodiamonds as being due to the diamonds interdiffusion and a formation of the graphite phase between the diamond crystallites.

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