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On Thermal Conductivity of Anisotropic Nanodiamond

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Dependence of thermal conductivity of nanocrystalline diamond coating on grain size and form is theoretically investigated. Nanodiamond is considered as two-phase material composed of dielectric diamond grains characterizing by three main dimensions and segregated by thin graphite layers with electron or phonon thermal conductivity. Influence of thermal conductance type and thickness of boundary layer on nanodiamond thermal conductivity is analysed. Derived dependences of thermal conductivity on grain dimensions are compared with experimental data.

Keywords: Anizotropic Nanodiamond Coating, Crystalline Grain, Boundary Layer, Thermal Conductivity

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1. INTRODUCTION

As it is known, monocrystalline diamond has the highest thermal conductivity within solid materials, On the contrary, low thermal conductivity of ultrananocrystalline diamond (UNCD) materials which is in several hundred times less than that of diamond requires special accounting at calculation of thermal conditions in processes where they are used [1,2]. In view of small sizes of grains they boundary layers substantially determine thermal properties of UNCD. Understanding of these properties and possibility to control them are very important for practical use of UNCD materials. Dependence of thermal conductivity of isotropic UNCD on effective size of grain was theoretically investigated in ref. [3]. However, derived formulas are inapplicable for calculation of thermal conductivity of anisotropic diamond coatings [4].

The goal of the paper is the theoretical investigation of dependence of thermal conductivity of anisotropic UNCD on characteristic dimensions of crystal grain and on boundary thickness.

2. METHOD OF ANALYSIS AND CALCULATION

Let nanodiamond is a composite consisting of diamond grains (sp^3-bond carbon) separated by thin graphite layers (sp^2-bond carbon). It can be supposed that graphite is amorphizing because of heightened imperfection of boundary layer. According to this conception one should determine thermal conductivity of nanodiamond as the corresponding value of a two-component composite material. To solve this problem we have to know some characteristics of each component and take into consideration how change these characteristics for nanometer-sized objects.

In the course of analysis we replace the real UNCD structure with the model one which includes all basic elements of heat transfer in two-component material.

Fig. 1 shows scheme of UNCD crystaline and equivalent modeling structure to be used for calculation of effective thermal conductivity of UNCD. Also, Fig. 1 shows the model of the elementary cell consisting of diamond gain surrounded with graphite shell which is marked by grey color. The shell thickness does not exceed 1 nm. We shall characterize the elementary cell by dimentions *X, Y, Z* of the diamond grain along three orthogonally related directions (x, y, z axes) and by boundary shell thickness *d*. We suppose that nanodiamond is an orthotropic material. It corresponds to properties of deposited UNCD coatngs possessing different grain dimentions in the plane of the coating and in perpendicular direction. In the general case, dimentions *X, Y, Z* are different.

The effective thermal conductivity λ^{ef} of orthotropic material is a second-rank tensor associating gradient of temperature T with heat flow density $\vec{q}$: $q_i = -\lambda_{ik}^{ef}\left(\partial T/\partial x_k\right)$. In Cartesian coordinate system x, y, z which is associated with *X, Y, Z* dimentions tensor λ^{ef} has only diagonal elements and the basic Fourier conduction law transforms to more simple form $q_x = -\lambda_x^{ef}\left(\partial T/\partial x\right)$; $q_y = -\lambda_y^{ef}\left(\partial T/\partial y\right)$; $q_z = -\lambda_z^{ef}\left(\partial T/\partial z\right)$, where λ_x^{ef}, λ_y^{ef} and λ_z^{ef} are the tensor eigenvalues which are equal to thermal-conductivity coefficient in direction of axes x, y, z, correspondingly. Determination of λ_x^{ef}, λ_y^{ef} и λ_z^{ef} permits to determine temperature field in UNCD material.

Diamond heat conduction has purely phonon nature and may be interpreted as diffusion of thermal phonons. The thermal conductivity of single crystal diamond connected with middle phonon path l by relation $\lambda = \rho C s l/3$, where ρ, C s are the mass

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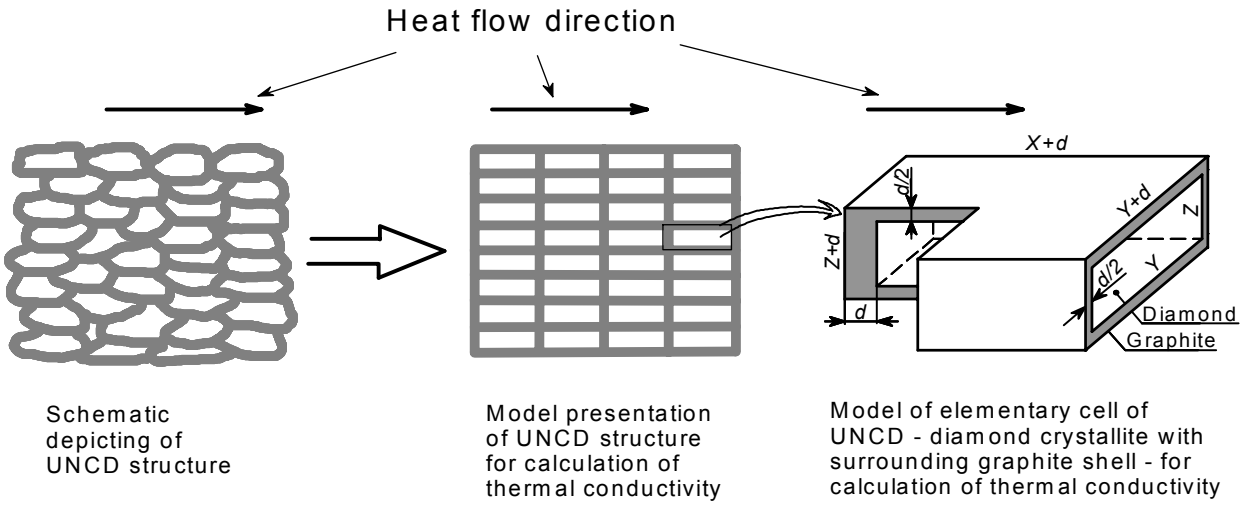

Fig. 1 – Scheme of UNCD crystalline and equivalent model structure to be used for effective thermal conductivity calculation. Isometric display of model grain is shown on the right.

density, the specific heat capacity, and the longitudinal sound velocity in single crystal diamond, correspondingly. Taking $\lambda \approx 2000$ W/(m·K) we get the next assessment for the middle phonon path: l = 220 nm. Obtained value may considerably exceed characteristic dimension of nanodiamond grain. Supposing that phonons are reflected on crystalline interface we conclude that characteristic dimension of nanodiamond grain is parameter determining the effective phonon path in nanodianond.

In case of orthotropic crystalline diamond the effective phonon path depends on direction. Particularly, one can use the following expression to determine the effective phonon path l_x in direction of *x*-axis: $l_x^{-1} = l^{-1} + (X/2)^{-1}$. Using this equation we can write expression for thermal conductivity of diamond phase along *x*-axis in form:

$$\lambda_x(X) = \frac{1}{3}\rho C s \cdot \frac{lX}{2l+X}, \qquad (2.1)$$

We can easily write similar expressions for thermal conductivity of diamond phase along *y*-axis and *z*-axis.

Equation (1) does not take into account dependence of thermal conductivity of crystalline diamond on thermal resistance of amorphous graphite layer between grains. At present this boundary resistance is unknown. As graphite is semimetal its thermal conductivity can be mainly conditioned by electron transport. In this case one can estimate value of thermal conductivity of boundary layer using formula $\kappa_b = l_e v_F/3$, where l_e is the free length of conduction electron with the Fermi energy ε_F. For graphite we can accept $\varepsilon_F = 0.026$ eV. Using formula $v_F = \sqrt{2\varepsilon_F/m_e}$, where m_e is electron mass we obtain $v_F \approx 10^5$ m/s. The free length of conduction electron at room temperature exceeds considerably the interatomic distance a: $l_e = (200...250)\cdot a$. Taking into account that thickness of boundary layer d is approximately equal to $2a$ we can put for the effective $l_e = d/2$. In this case thermal conductivity of boundary layer material is equal to:

$$\lambda_b(d) \approx \rho_G C_G \frac{dv_F}{6}, (d \geq 2a), \qquad (2.2)$$

where ρ_G and C_G, are the mass density and the specific heat capacity of graphite, corresponingly.

Thus we see that thermal conductivity of boundary layer is directly proportional to layer thickness d if the heat transfer is conditioned by electron transport.

If thermal conductivity of boundary layer depends on phonon transport then one should make double replacement in equation (2): $d \to 2a$; $v_F \to s$. Here $s \approx 1{,}5\cdot 10^3$ m/s is the longitudinal sound velocity in graphite. It is easy to see, that the phonon conductivity $\lambda_b(d) = \rho_G C_G a s/3$ is considerably less (in ~70 times) than the electronic one and does not depend on thickness of boundary layer. In the general case, both mechanisms can contribute to heat conductance of boundary layer depending on a coating growth process, doping, etc. Hence, thermal conductivity of boundary layer can possess any value from interval determined by both above mechanisms.

Let's determine effective thermal conductivity of UNCD taking into consideration the effect of boundary layer. Applying the basic Fourier conduction law to heat transport of elementary cell, as it was made in [3], we obtain the following expression for the effective λ_x^{ef} in direction of x-axis:

$$\lambda_x^{ef}(X,d)=\lambda_b(d)\left[1+\frac{XYZ\left[\lambda_x(X)-\lambda_b(d)\right]}{\left(\lambda_b(d)X+\lambda_x(X)d\right)(Y+d)(Z+d)}\right] \tag{2.3}$$

We can get analogous expressions for thermal conductivities along y- and z-axes directions by circular permutations $X\to Y\to Z\to X$.

3. CALCULATION RESULTS AND DISCUSSION

Assuming $X=Y=Z$in (3) we get expression for thermal conductivity of isotropic bi-component material [3]:

$$\lambda^{ef}(X,d)=\lambda_b(d)\left[1+\frac{X^3\left(\lambda_x(X)-\lambda_b(d)\right)}{\left(\lambda_b(d)X+\lambda_x(X)d\right)(X+d)^2}\right]$$

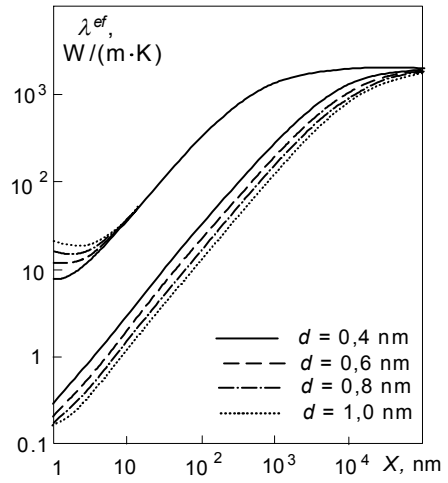

Fig. 2 - Dependence of effective thermal conductivity λ^{ef} of UNCD on grain size X of isotropic nanodiamond at different thicknesses of boundary layer d. Upper (lower) group of curves corresponds to electron (phonon) thermal conductivity of boundary layer

Obtained expression physically reasonably represents dependence of thermal conductivity of composite material on component parameters. Particularly, the effective thermal conductivity tents to zero (to infinity) at $\lambda_b\to 0\,(\lambda_b\to\infty)$. It takes place because the boundary layer plays role of binding agent or matrix into which embed diamond grains which are thermally isolated one from another. That is why the effective thermal conductivity does not tent to zero (to infinity) at $\lambda_x\to 0\ (\lambda_x\to\infty)$. Thus, influence of components in considered case is nonequivalent. That is why the expression is asymmetric relatively double replacement $\lambda_b\rightleftarrows\lambda_x$ and $X\rightleftarrows d$. Also, we have $\lambda_x^{ef}=\lambda_x$ at $\lambda_b=\lambda_x$, and $\lambda_x^{ef}\to\lambda_b$ at $X\to 0$ that corresponds to transfer to homogeneous material.

Fig. 2 illustrates dependence of effective thermal conductivity λ^{ef} of isotropic UNCD on grain dimension X at different thicknesses d of boundary layer. Calculation was performed for two kinds of thermal conductivity of boundary layer, namely, electron (upper group of curves) and phonon (lower group of curves) thermal conductivity.

In case of electron nature of thermal conductivity the boundary layer thickness influences on UNCD thermal conductivity λ_{ef} only at ultimately small grain sizes X < 10 nm, and λ_{ef} increases with d. In case of phonon mechanism domination λ^{ef} decreases with d in all range of grain sizes X. The phonon path l in the grain material practically does not influences on λ^{ef} at $X\le l$. Calculation shows (see Fig. 2) that UNCD thermal conductiviry at grain sizes 2…10 nm can be less than 10 W/(m·K) in accordance with experimental data [2] whereas thermal conductivity of polycrystalline coating is equal to 1800…2200 W/(m·K).

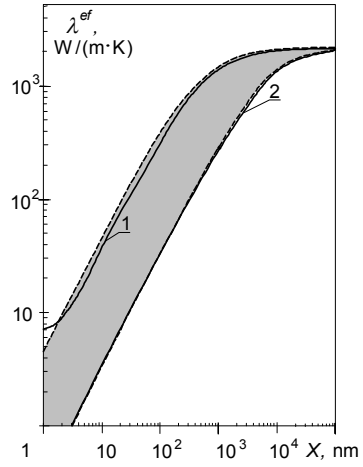

Fig. 3 - Range of UNCD thermal conductivity, determined from experimental data [5] (area limited by dashed curves and marked by grey color). Solid curves 1,2 are dependences $\lambda^{ef}(X)$ for isotropic UNCD calculated at electron (curve 1) and phonon (curve 2) thermal conductivity of boundary layer.

Fig.3 displays the range where experimentally determined values of thermal conductivity lie (area bounded by dashed curves and marked by grey color) [5]. Solid curve 1 shows dependence $\lambda^{ef}(X)$ for isotropic nanodiamond made in supposition of electron thermal conductivity of boundary layer. Solid curve 2 shows dependence $\lambda^{ef}(X)$ corresponding to case of phonon thermal conductivity of boundary layer. The thickness d is equal to 2a ≈ 0.36 nm in both cases. As it can see from figure the analytical results do not contradict to experimental observations. If thermal conductivity of boundary layer includes depositions both electron and phonon transport then curve $\lambda^{ef}(X)$ will lie between curves 1 and 2 in marked range.

At present time experimental data on thermal conductivity of UNCD in the range of ultimately small grain sizes X ~ 1 nm where influence of boundary layer appears are very poor. Such data could clarify nature of thermal conductivity of boundary layer

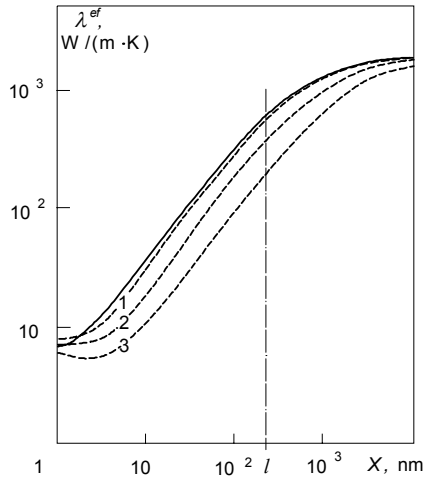

Fig. 4 - Thermal conductivities $\lambda_x^{ef}, \lambda_y^{ef}, \lambda_z^{ef}$ of orthotropic nanodoamond with the following proportion of grain dimensions $X : Y : Z = 1 : 0.5 : 0.25$ (dashed curves 1, 2, 3, respectively). Solid curve is dependence $\lambda^{ef}(X)$ for isotropic nanodiamond ($X = Y = Z$).

Let nanodiamond grain is characterized by different dimensions X, Y, Z . In this case all tensor eigenvalues are different. Fig. 4 shows fuctions $\lambda_x^{ef}(X)$, $\lambda_y^{ef}(X)$, $\lambda_z^{ef}(X)$ in case when the following proportion between grain dimensions takes place $X : Y : Z = 1 : 0.5 : 0.25$ (dashed curves 1, 2, 3, respectively). Solid curve corresponds to the effective thermal conductivity of isotropic UNCD. Thermal conductivity of boundary layer was calculated by equation (3) i.e., has electron nature. As it can see from Fig. 4, anisotropy considerably influences on value of thermal conductivity in different directions. One need to take into account this effect at calculation of thermal conditions of devices based on nanocrystalline coatings.

4. CONCLUSIONS

1. In the model describing structure of orthotropic crystalline diamond by four parameters - effective dimentions *X, Y, Z* of the diamond grain and boundary shell thickness *d* - expressions for eigenvalues of thermal conductivity tensor were derived. Obtained expressions provide physically grounded characterization of UNCD thermal conductivity in the vast range of grain dimensions from 1 nm and more. Calculation shows that anisotropy considerably influences on value of thermal conductivity in different directions.

2. According to derived model thermal conductivity of isotropic UNCD increases with grain size from 5 W/(m·K) to 2200 W/(m·K). The last corresponds to thermal conductivity of polycrystalline diamond at $X > 10^3$ nm.

3. Influence of boundary layer on UNCD thermal conductivity λ^{ef} depends considerably on nature of its thermal conductivity. In case of electron thermal conductivity domination the boundary layer thickness *d* affect λ^{ef} only at grain sizes $X < 10$ nm, and λ^{ef} increases with *d*. In case of phonon thermal conductivity domination UNCD thermal conductivity λ^{ef} decreases with *d* in all range of grain sizes *X*.

4. Obtained in the model values of thermal conductivity as well as their behavior depending on grain size in case of isotropic UNCD are in accordance with known experimental data. For thorough testing proposed model one should carry out thermal conductivity measurements in range of grain sizes from 1 nm to 100 nm at reliable controlling thickness of boundary layer.

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