Theoretical model for calculation of elastic coefficients of composite materials based on polycrystalline diamond and cubic boron nitride

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1. Introduction

Superhard materials based on polycrystalline cubic boron nitride (CBN) and diamond (PCD) were developed in the 70-ties of the last century. The most important features of these materials are very high hardness and wear resistance. Due to these properties they are widely used for high quality cutting tools, drilling bits and wire drawing dies.

Diamond is the first and cubic boron nitride the second hardest material known. As single crystals they are hard but susceptible to cleavage along certain crystallographic planes. This propensity for cleavage can be greatly reduced in polycrystalline materials containing a big number of randomly oriented grains. It is the main idea which led to the development of superhard polycrystalline materials based on diamond or CBN.

Production process of such materials involves high-pressure (5-8 GPa), high-temperature (1500-2300°C) sintering of diamond or CBN powder mixed with specially selected binder-catalyst phase. The material produced in this process is a composite containing grains of diamond or boron nitride surrounded by a softer binder-catalyst phase. Macroscopic properties of such materials depend on the proportion of superhard to binder phase as well as on the arrangement of the two phases within the material. One of the most important structural features is presence of direct bonding (bridges) between grains of superhard phase.

CBN and PCD composites present considerable difficulties for conventional material testing methods. They are produced in the form of cylindrical compacts which sizes are too small to prepare samples for standard mechanical tests. Special techniques for determination of tensile strength, transverse rupture strength and fracture toughness have been developed but due to their complexity and destructive character they have very limited application.

In view of these problems ultrasonic method became one of the most important testing techniques for PCD and CBN superhard materials. Ultrasonic techniques can be used for detection of defects in sintered compacts as well as for determination of elastic constants of their material. Elastic properties of composite material are directly related to its composition and microstructure. The correlation can be established on the bases of comparative experimental measurements or from the theoretical models.

Some authors have already tried to correlate ultrasonically measured elastic constants of PCD and CBN materials with their composition and grain size. Lammer [1] established some empirical relation between diamond grain size, content of cobalt binder phase and elastic modulus for PCD materials.

D'Evelyn and Taniguchi [2] have measured the elastic constants of several grades of PCD and CBN materials and compared the results with theoretical values calculated from the Hershey–Kröner–Eshelby equation. Their experimental results showed that elastic moduli of the considered materials were strongly dependent on the content of binder phase. On the other hand the Hershey–Kröner–Eshelby equation allows for calculation of theoretical moduli only for pure polycrystalline materials (without any content of binder phase). Clearly, this model didn't account for a very important feature of PCD and CBN composites i.e. dependence of their macroscopic properties on the type and amount of binder-catalyst phase.

Another limitation of existing works on elastic properties of superhard composites is commonly adopted assumption about their macroscopic isotropy. This assumption was essential in experimental determination of elastic moduli from ultrasonic and resonance measurements [1, 2]. However it should be noted that PCD and CBN composites are sintered in high pressure apparatus which create rather axially symmetric then isotropic stress state. Such non-hydrostatic stress can cause non-uniform orientation distribution of crystalline grains (texture) leading to macroscopic material anisotropy. Such anisotropy was found in many polycrystalline materials and should be taken into account also in case of PCD and CBN composites. The correlation between texture and the elastic constants of macroscopic samples can be investigated on the base of a proper theoretical model.

2. Formulation of the problem

The macroscopic elastic properties of PCD and CBN composites can be determined by measurements of ultrasonic velocities or by dynamic resonance method. The measured values of elastic constants can be interpreted in terms of composition and microstructural features of considered materials. To this effect various theoretical models of composite material can be adopted.

The main aim of the present work is to develop a theoretical model of composite material enabling calculation of macroscopic elastic constants on the bases of phase composition and texture. The modelled material consist of predominant superhard phase (diamond or cubic boron nitride) and additional binder-catalyst phase. It will be assumed that the material possesses axial symmetry imposed by sintering conditions. From the microscopic point of view it means that statistical orientation distribution of constituent crystallites has cylindrical symmetry around a technological axis.

The proposed model overcomes the main limitations of Hershey–Kröner–Eshelby solution in case of PCD and CBN composites. First of all it accounts for the effect of binder-catalyst phase and gives the possibility to calculate elastic constants for different grades of superhard materials with any content of binder phase. Such theoretical values can be considered as a reference points for elastic constants measured on real samples.

The second aspect of the proposed model is that it takes into account the textural anisotropy of PCD and CBN materials. It enables to find the anisotropic elastic constants on the basis of orientation distribution function (ODF) of its constituent crystallites. It can be also useful in elaboration of experimental data concerning elastic constants of superhard materials.

The basic assumptions of the proposed model are summarised below:

- The modelled material is composed of crystalline grains of cubic symmetry (diamond or cubic boron nitride) surrounded by perfectly isotropic binder-catalyst phase.

- The sizes of the crystalline grains are uniform in all directions and are much smaller than dimensions of the macroscopic sample.

- The material posses cylindrical symmetry around technological axes caused by non-uniform orientation distribution of constituent crystallites (texture).

- The macroscopic elastic constants are calculated as Voigt, Reuss and Hill averages over the crystalline grains and binder phase volumes.

- Averaging over different orientations of crystalline grains is performed with the weighting function given by orientation distribution function (ODF) possessing cylindrical symmetry.

The application of relatively simple Voigt, Reuss and Hill averaging pro-
cedures (so called VRH model) for the calculation of effective eastic con-
stants of considered materials is justified by the results of previous works on
single phase, isotropic polycrystalline materials. Sisodia et al. [3] reviewed
available data for a few tens of polycrystalline materials and concuded that
Hill's averaging procedure had given elastic modulus in good agreement with
solutions of Hershey–Kröner–Eshelby equation and with experimental data.
Based on these results it can be expected that VRH model will give reason-
able approximation of elastic constants also for anisotropic polycrystalline
composites.

Another advantage of the VRH model is fact that it can be easily gener-
alized for multi-phase materials with non-random orientation distribution of
grains. In this way two important characteristics of the real PCD and CBN
composites can be included in the theoretical model.

3. Orientation distribution function

Quantitative description of texture in polycrystalline material requires
knowledge of orientation distribution function $w(\psi, \theta, \varphi)$ of crystalites in the
macroscopic sample. The orientation of individual crystallite in the sample
coordinate system is specified by the three Euler angles: θ, ψ, ρ [4]. The
angles specify the consecutive rotations of crystallite-fixed coordinate system
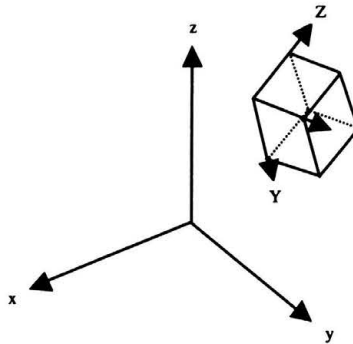X, Y, Z with respect to sample-fixed coordinate system x, y, z.

FIGURE 1. Crystallite coordinate system X, Y, Z with respect to sample coordi-
nate system x, y, z.

The orientation distribution function $w(\xi, \psi, \varphi)$, where $\xi = \cos \theta$, is de-
fined as the probability of finding a crystallite having an orientation specified
by the angles ξ, ψ, φ with respect to the sample coordinate system. The inte-

gration of this probability function over all possible orientations must satisfy:

$$\int\limits_0^{2\pi} \int\limits_0^{2\pi} \int\limits_{-1}^{1} w(\xi, \psi, \varphi) \, d\xi \, d\psi \, d\varphi = 1. \tag{3.1}$$

According to mathematical formalism developed by Roe [4], the orientation distribution function $w(\xi, \theta, \varphi)$ can be expanded in a series of generalized spherical harmonics as:

$$w(\xi, \psi, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{n=-l}^{l} W_{lmn} Z_{lmn}(\xi) \, e^{-im\psi} \, e^{-in\varphi}, \tag{3.2}$$

where $Z_{lmn}(\xi)$ is the generalisation of the associated Legendre functions defined in [4] and W_{lmn} are expansion coefficients given by:

$$W_{lmn} = \frac{1}{4\pi^2} \int\limits_0^{2\pi} \int\limits_0^{2\pi} \int\limits_{-1}^{1} w(\xi, \psi, \varphi) \, Z_{lmn}(\xi) \, e^{im\psi} \, e^{in\varphi} d\xi \, d\psi \, d\varphi. \tag{3.3}$$

From the fact that all crystal classes posses inversion symmetry it can be shown that in the expansion series (3.2) all coefficients W_{lmn} with l odd must vanish. The expression (3.2) can be further simplified by considering specific symmetry requirements assumed for our model in Section 2.

The cylindrical symmetry imposed on the orientation distribution function requires that $w(\psi, \theta, \varphi)$ should be independent of angle θ. Consequently all the expansion coefficients with $m \neq 0$ must vanish:

$$\begin{aligned} W_{lmn} &\neq 0, \qquad m = 0 \\ W_{lmn} &= 0, \qquad m \neq 0. \end{aligned} \tag{3.4}$$

The cubic symmetry of constituent crystallites imposes another set of restrictions on W_{lmn}. Fourfold rotation symmetry around the crystallographic Z-axis yields:

$$\begin{aligned} W_{lmn} &\neq 0, \qquad n = 4k \\ W_{lmn} &= 0, \qquad n \neq 4k, \qquad k \in C. \end{aligned} \tag{3.5}$$

From the twofold symmetry around X or Y crystal axis we conclude that for all nonzero W_{lmn} we have:

$$W_{lmn} = W_{lm\bar{n}}, \quad \text{where} \quad \bar{n} = -n. \tag{3.6}$$

Fourfold rotational symmetry around X or Y crystallographic axis leads to additional linear relations between nonzero coefficients W_{lmn} [5]. For a few lower values of index l they can be explicit written as:

$$\text{for } l = 2 \qquad W_{200} = 0,$$

$$\text{for } l = 4 \qquad W_{404} = \frac{5}{\sqrt{70}} W_{400}, \qquad (3.7)$$

$$\text{for } l = 6 \qquad W_{604} = -1.8708\, W_{600}.$$

Taking into consideration all the above symmetry conditions for W_{lmn} the expansion series (3.2) may be rewritten in a much simplified form:

$$
\begin{aligned}
w(\xi, \psi, \varphi) = \; & W_{000} Z_{000}(\xi) + W_{400} Z_{400}(\xi) + W_{40\bar{4}}\, Z_{40\bar{4}}(\xi) e^{-i4\varphi} \\
& + W_{404}\, Z_{404}(\xi) e^{i4\varphi} + W_{600} Z_{600}(\xi) + W_{60\bar{4}}\, Z_{60\bar{4}}(\xi) e^{-i4\varphi} \\
& + W_{604}\, Z_{604}(\xi) e^{i4\varphi} + \ldots, \qquad (3.8)
\end{aligned}
$$

where

$$
\begin{aligned}
W_{000} &= \frac{1}{4\sqrt{2}\pi^2}, \\
W_{40\bar{4}} &= W_{404} = \frac{5}{\sqrt{70}}\, W_{400}, \qquad (3.9) \\
W_{60\bar{6}} &= W_{606} = -1.8708\, W_{600}, \quad \text{etc.}
\end{aligned}
$$

In spite of considerable reduction of terms in expansion series (3.8) their number is still infinite. It will be shown that using the VRH averaging procedure only the terms up to $l = 4$ do not vanish. It means that the elastic anisotropy of considered materials can be fully described by only one parameter of crystallographic texture; namely the coefficient W_{400} of the ODF expansion series. It should be noted however that this important conclusion is valid only for materials composed of cubic crystallites which are distributed according to ODF function possessing cylindrical symmetry.

4. Calculation of averaged elastic constants

4.1. Voigt averaging procedure

In Voigt-type averaging procedure it is assumed that effective elastic constants of polycrystalline material are calculated as an average of single crystal elastic constants over all possible orientations of crystalline grains with ODF function as a weighting function. The procedure, in the case of single phase polycrystalline aggregates, was described by Pursey and Cox [6], Sayers [10]

and Hirao and others [12]. In the present work the Voigt-type averaging procedure is modified by extension of the averaging integrals over the second, binder-catalyst phase. Mathematically it can be expressed by the formula:

$$c_{ij}^{kV} = V < c_{ij}' > + (1 - V)\, c_{ij}^b, \qquad (4.1)$$

where:

c_{ij}' – the elastic constants of a crystalline grain referred to the macroscopic coordinate system of the sample,

$< c_{ij}' >$ – average of the elastic constants over the orientation distribution of grains,

c_{ij}^b – elastic constants of isotropic binder-catalyst phase,

V – volume fraction of superhard phase in the composite material.

The directional averaging over the binder-catalyst phase is avoided because of the simplifying assumption that this phase is perfectly isotropic. The averaging over orientation distribution of superhard phase is expressed by the formula:

$$< c_{ij}' > = \int_0^{2\pi} \int_0^{2\pi} \int_{-1}^{1} w(\xi, \psi, \varphi)\, c_{ij}'(\xi, \psi, \varphi)\, d\xi\, d\psi\, d\varphi, \qquad (4.2)$$

where the notation $c_{ij}'(\xi, \psi, \varphi)$ formally shows the dependence of elastic constants of the crystallite on its orientation with respect to the global sample axis.

To obtain the explicit form of this dependence we have to transform the single-crystal elastic constants of a grain from its crystallographic coordinates XYZ to the global coordinates xyz. This transformation may be accomplished by the Bond matrix formalism described by Auld [7].

In this approach the single-crystal elastic constants matrix $[c_{ij}']$ referred to the global coordinate system is obtained from the basic elastic constants matrix $[c_{ij}]$ referred to crystallographic axes by simple matrix multiplication: left side with the Bond matrix $[M]$ and right side with its transposition $[M]^T$:

$$[c_{ij}'] = [M][c_{ij}][M]^T. \qquad (4.3)$$

The basic elastic constant matrix for cubic crystals has the well-known form:

$$[c_{ij}] = \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{bmatrix}. \qquad (4.4)$$

The Bond matrix $[M]$ is defined as follows:

$$[M] = \begin{bmatrix} l_1^2 & l_2^2 & l_3^2 & 2l_2l_3 & 2l_1l_3 & 2l_1l_2 \\ m_1^2 & m_2^2 & m_3^2 & 2m_2m_3 & 2m_1m_3 & 2m_1m_2 \\ n_1^2 & n_2^2 & n_3^2 & 2n_2n_3 & 2n_1n_3 & 2n_1n_2 \\ n_1m_1 & n_2m_2 & n_3m_3 & m_2n_3+n_2m_3 & m_1n_3+n_1m_3 & m_1n_2+m_2n_1 \\ l_1n_1 & l_2n_2 & l_3n_3 & l_2n_3+l_3n_2 & l_1n_3+n_1l_3 & l_1n_2+l_2n_1 \\ l_1m_1 & l_2m_2 & l_3m_3 & l_2m_3+m_2l_3 & l_1m_3+l_3m_1 & l_1m_2+m_1l_2 \end{bmatrix},$$

where l_1, l_2, l_3, m_1, m_2, m_3, n_1, n_2, n_3 are the direction cosines of global coordinate axis x,y,z expressed in crystallite-fixed coordinate system XYZ.

These directional cosines can be easily expressed in terms of the Euler angles (ψ, θ, φ) defining the rotations which transforms the global coordinate system xyz into the crystallite-fixed coordinate system XYZ:

$$l_1 = -\sin\psi\sin\phi + \cos\psi\cos\phi\cos\theta,$$
$$l_2 = -\sin\psi\cos\phi - \cos\psi\sin\phi\cos\theta,$$
$$l_3 = \sin\theta\cos\psi,$$

$$m_1 = \cos\psi\sin\phi + \sin\psi\cos\phi\cos\theta,$$
$$m_2 = \cos\psi\cos\phi - \sin\psi\sin\phi\cos\theta, \qquad (4.5)$$
$$m_3 = \sin\theta\sin\psi$$

$$n_1 = -\sin\theta\cos\phi,$$
$$n_2 = \sin\theta\sin\phi - \cos\psi\sin\phi\cos\theta,$$
$$n_3 = \cos\theta.$$

The execution of prescribed stiffness matrix transformation is straightforward but rather tedious. Below, we give the final expressions for some of the transformed elastic constants (the other are not necessary because their averages over orientation distribution function can be deduced from the condition of transversal isotropy of the composite material):

$$c'_{11} = c_{11} - 2c\,(l_1^2l_2^2 + l_1^2l_3^2 + l_2^2l_3^2),$$
$$c'_{33} = c_{11} - 2c\,(n_1^2n_2^2 + n_1^2n_3^2 + n_2^2n_3^2),$$
$$c'_{44} = c_{44} + c\,(m_1^2n_1^2 + m_2^2n_2^2 + m_3^2n_3^2), \qquad (4.6)$$
$$c'_{12} = c_{12} + c\,(l_1^2m_1^2 + l_2^2m_2^2 + l_3^2m_3^2),$$
$$c'_{13} = c_{12} + c\,(l_1^2n_1^2 + l_2^2n_2^2 + l_3^2n_3^2),$$

where $c = c_{11} - c_{12} - 2c_{44}$.

All transformed elastic moduli depend on the orientation of the crystallite through direction cosines: l_i, m_i, n_i which, in turn, are trigonometric functions of Euler angles (ψ, θ, φ). To emphasize this dependence we introduce auxiliary functions $r_i(\xi, \psi, \varphi)$ defined as follows:

$$
\begin{aligned}
r_1 &= l_1^2 l_2^2 + l_1^2 l_3^2 + l_2^2 l_3^2, \\
r_3 &= n_1^2 n_2^2 + n_1^2 n_3^2 + n_2^2 n_3^2, \\
r_4 &= m_1^2 n_1^2 + m_2^2 n_2^2 + m_3^2 n_3^2, \\
r_6 &= l_1^2 m_1^2 + l_2^2 m_2^2 + l_3^2 m_3^2, \\
r_5 &= l_1^2 n_1^2 + l_2^2 n_2^2 + l_3^2 n_3^2.
\end{aligned}
\tag{4.7}
$$

Using these functions the averages of single-crystal elastic moduli over the crystallite orientation distribution function can be written in the following form:

$$
\begin{aligned}
< c_{11}' > &= c_{11} - 2c < r_1 >, \\
< c_{33}' > &= c_{11} - 2c < r_3 >, \\
< c_{44}' > &= c_{44} + c < r_4 >, \\
< c_{12}' > &= c_{12} + c < r_6 >, \\
< c_{13}' > &= c_{12} + c < r_5 >,
\end{aligned}
\tag{4.8}
$$

where unknown averages of functions $r_i(\xi, \psi, \phi)$ are given by the integrals of the type:

$$
< r_i > = \int\limits_0^{2\pi} \int\limits_0^{2\pi} \int\limits_{-1}^1 w(\xi, \psi, \varphi)\, r_i(\xi, \psi, \varphi)\, d\xi\, d\psi\, d\varphi.
\tag{4.9}
$$

The functions $r_i(\xi, \psi, \varphi)$ can be expanded in the series of generalized spherical harmonics in exactly the same way as the orientation distribution function $w(\xi, \psi, \varphi)$:

$$
r_i(\xi, \psi, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{n=-l}^{l} R_{lmn}^{(i)} Z_{lmn}(\xi)\, e^{-im\psi} e^{-in\varphi},
\tag{4.10}
$$

where the expansion coefficients are given by:

$$
R_{lmn}^{(i)} = \frac{1}{4\pi^2} \int\limits_0^{2\pi} \int\limits_0^{2\pi} \int\limits_{-1}^1 r_i(\xi, \psi, \varphi)\, Z_{lmn}(\xi)\, e^{im\psi} e^{in\varphi} d\xi\, d\psi\, d\varphi.
\tag{4.11}
$$

Expanding both functions in the integral (4.9) in the generalized spherical harmonics series and utilizing the orthogonal relations between harmonics we obtain:

$$< r_i >= 4\pi^2 \left(\sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{n=-l}^{l} R_{lmn}^{(i)} W_{lmn} \right). \qquad (4.12)$$

The remaining problem to solve is calculation of expansion coefficients $R_{lmn}^{(i)}$. Analysing the expressions (4.7) and (4.5) we can see that $r_i(\xi, \psi, \varphi)$ contain trigonometric functions with at most fourth powers of $\cos\theta$ or $\sin\theta$. Taking into consideration the properties of generalized spherical harmonics it can be shown that in the expansion series (4.10) only terms up to $l = 4$ are nonzero. Formally it can be expressed as:

$$R_{lmn}^{(i)} = 0 \quad \text{for} \quad l > 4. \qquad (4.13)$$

It means that the series (4.12) is truncated at $l = 4$. Because of the discussed earlier symmetry requirements concerning W_{lmn}, the series can be further simplified to the form:

$$< r_i > = \tfrac{1}{\sqrt{2}} R_{000}^{(i)} + 4\pi^2 \left[R_{400}^{(i)} + \tfrac{5}{\sqrt{70}} \left(R_{404}^{(i)} + R_{40\bar{4}}^{(i)} \right) \right] W_{400}. \qquad (4.14)$$

The calculation of all required terms $R_{000}^{(i)}$, $R_{400}^{(i)}$, $R_{404}^{(i)}$, $R_{40\bar{4}}^{(i)}$ can be done by using the integrals (4.11). After substitution of the results into (4.14) we finally obtain:

$$< r_1 > = \frac{1}{5} - \frac{6\sqrt{2}\pi^2}{35} W_{400},$$

$$< r_3 > = \frac{1}{5} - \frac{16\sqrt{2}\pi^2}{35} W_{400},$$

$$< r_4 > = \frac{1}{5} - \frac{6\sqrt{2}\pi^2}{35} W_{400}, \qquad (4.15)$$

$$< r_5 > = \frac{1}{5} - \frac{16\sqrt{2}\pi^2}{35} W_{400},$$

$$< r_6 > = \frac{1}{5} + \frac{4\sqrt{2}\pi^2}{35} W_{400}.$$

Next, introducing $<r_i>$ into (4.8), we get the averaged stiffness moduli of the polycrystalline phase of the composite and then, using (4.1), the effective

stiffness coefficients for the whole composite:

$$c_{11}^{kV} = V\left(c_{11} - 2c < r_1 >\right) + (1 - V)\,c_{11}^{b},$$

$$c_{33}^{kV} = V\left(c_{33} - 2c < r_3 >\right) + (1 - V)\,c_{11}^{b},$$

$$c_{44}^{kV} = V\left(c_{44} + c < r_4 >\right) + (1 - V)\,c_{44}^{b}, \qquad (4.16)$$

$$c_{12}^{kV} = V\left(c_{12} + c < r_6 >\right) + (1 - V)\,c_{12}^{b},$$

$$c_{13}^{kV} = V\left(c_{12} + c < r_5 >\right) + (1 - V)\,c_{12}^{b},$$

where $c = c_{11} - c_{12} - 2c_{44}$, and:

c_{ij} – the stiffness moduli of superhard phase (as for single-crystal),

V – the volume fraction of superhard phase in the composite,

c_{ij}^{b} – the stiffness moduli of binder phase,

c_{ij}^{kV} – the effective stiffness moduli of the composite in the Voigt model.

As can be seen the effective stiffness moduli of the composite in the Voigt model depend on the stiffness moduli and volume fractions of both components as well as on the texture parameter W_{400} of polycrystalline phase.

The stiffness matrix of the composite has the form characteristic for a medium with transversal isotropy:

$$[c^{kV}] = \begin{bmatrix} c_{11}^{kV} & c_{12}^{kV} & c_{13}^{kV} & 0 & 0 & 0 \\ c_{12}^{kV} & c_{11}^{kV} & c_{13}^{kV} & 0 & 0 & 0 \\ c_{13}^{kV} & c_{13}^{kV} & c_{33}^{kV} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44}^{kV} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44}^{kV} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66}^{kV} \end{bmatrix}, \qquad (4.17)$$

where $c_{66}^{kV} = \frac{1}{2}(c_{11}^{kV} - c_{12}^{kV})$.

4.2. Reuss averaging procedure

In Reuss-type estimation procedure it is assumed that the effective compliance coefficients of a polycrystalline material are calculated as an average of single-crystal compliance moduli over all possible orientations of crystalline grains with ODF as a weighting function. In the present work the Reuss estimation is modified by extension of the averaging integrals over the second, binder-catalyst phase. Mathematically, it can be expressed by the formula:

$$s_{ij}^{kV} = V < s_{ij}' > + (1 - V)\,s_{ij}^{b} \qquad (4.18)$$

where:

s'_{ij} – the compliance moduli of a crystalline grain referred to the macroscopic coordinate system of the sample,

$< s'_{ij} >$ – average of the compliance constants over the orientation distribution of grains,

s^b_{ij} – compliance moduli of isotropic binder-catalyst phase,

V – the volume fraction of the superhard phase in the composite material.

The calculation algorithm of the Reuss model is now similar to the algorithms described earlier for the Voigt approach. The main difference is that now we have to average the single-crystal compliance moduli s_{ij} instead of single-crystal stiffness moduli c_{ij}. Because of that we have to use a slightly different Bond transformation matrix for transformation of single-crystal compliance moduli from the crystallographic coordinate system XYX to the sample fixed coordinate system xyz:

$$[s'_{ij}] = [N][s_{ij}][N]^{\mathrm{T}}. \tag{4.19}$$

The Bond matrix $[N]$ is defined as follows:

$$[N] = \begin{bmatrix}
l_1^2 & l_2^2 & l_3^2 & l_2l_3 & l_1l_3 & l_1l_2 \\
m_1^2 & m_2^2 & m_3^2 & m_2m_3 & m_1m_3 & m_1m_2 \\
n_1^2 & n_2^2 & n_3^2 & n_2n_3 & n_1n_3 & n_1n_2 \\
2n_1m_1 & 2n_2m_2 & 2n_3m_3 & m_2n_3+n_2m_3 & m_1n_3+n_1m_3 & m_1n_2+m_2n_1 \\
2l_1n_1 & 2l_2n_2 & 2l_3n_3 & l_2n_3+l_3n_2 & l_1n_3+n_1l_3 & l_1n_2+l_2n_1 \\
l_1m_1 & 2l_2m_2 & 2l_3m_3 & l_2m_3+m_2l_3 & l_1m_3+l_3m_1 & l_1m_2+m_1l_2
\end{bmatrix},$$

where l_1, l_2, l_3, m_1, m_2, m_3, n_1, n_2, n_3 are direction cosines of global coordinate axis x,y,z expressed in crystallite-fixed coordinate system XYZ.

Performing the prescribed compliance matrix transformation followed by averaging over orientation distribution function ODF is very similar to for Voigt appraoch and leads to the following expressions:

$$\begin{aligned}
< s'_{11} > &= s_{11} - 2s < r_1 >, \\
< s'_{33} > &= s_{11} - 2s < r_3 >, \\
< s'_{44} > &= s_{44} + 4s < r_4 >, \\
< s'_{12} > &= s_{12} + s < r_6 >, \\
< s'_{13} > &= s_{12} + s < r_5 >,
\end{aligned} \tag{4.20}$$

where $s = s_{11} - s_{12} - \frac{1}{2}s_{44}$, and $< r_i >$ are given by (4.15).

Final expressions for the effective compliance coefficients for the composite material obtained by using the Reuss approach are given by:

$$s_{11}^{kR} = V\left(s_{11} - 2s < r_1 >\right) + (1 - V)\, s_{11}^{b},$$

$$s_{33}^{kR} = V\left(s_{33} - 2s < r_3 >\right) + (1 - V)\, s_{11}^{b},$$

$$s_{44}^{kR} = V\left(s_{44} + 4s < r_4 >\right) + (1 - V)\, s_{44}^{b}, \qquad (4.21)$$

$$s_{12}^{kR} = V\left(s_{12} + s < r_6 >\right) + (1 - V)\, s_{12}^{b},$$

$$s_{13}^{kR} = V\left(s_{12} + s < r_5 >\right) + (1 - V)\, s_{12}^{b}.$$

where $s = s_{11} - s_{12} - \frac{1}{2}s_{44}$, and:

s_{ij} – the compliance moduli of superhard phase (as for single-crystal),

V – the volume fraction of superhard phase in the composite,

s_{ij}^{b} – the compliance moduli of isotropic binder phase,

s_{ij}^{kR} – the effective compliance coefficients of the composite in the Reuss model.

The last step of calculations is the conversion the above compliance matrix into stiffness matrix of the composite. It can be accomplished by the standard formula given, for example, by Auld [7]:

$$c_{11}^{kR} = \frac{s_{33}^{kR}}{2\beta} + \frac{1}{2\left(s_{11}^{kR} - s_{12}^{kR}\right)},$$

$$c_{33}^{kR} = \frac{s_{11}^{kR} + s_{12}^{kR}}{\beta},$$

$$c_{44}^{kR} = \frac{1}{s_{44}^{kR}}, \qquad (4.22)$$

$$c_{12}^{kR} = \frac{s_{33}^{kR}}{2\beta} - \frac{1}{2\left(s_{11}^{kR} - s_{12}^{kR}\right)},$$

$$c_{13}^{kR} = -\frac{s_{13}^{kR}}{\beta},$$

where:

$\beta = s_{33}^{kR}(s_{11}^{kR} + s_{12}^{kR}) - 2(s_{13}^{kR})^2$,

c_{ij}^{kR} – the effective stiffness moduli of the composite.

The form of this stiffness matrix is exactly the same as the one given in (4.17) by using Voigt's approach.

4.3. The Hill average

It is well-known that both Voigt and Reuss averaging procedures are based on non-physical assumptions concerning the stress/strain state within the multi phase or polycrystalline material.

In case of the Voigt approach it is assumed that strain state is uniform across the material what is clearly false because to achieve such condition some external forces would be required on the grain boundaries to keep it in balance.

On the other hand, in the Reuss approach, it is assumed that stress state is uniform in the material what clearly leads to material disruptions at the grain boundaries (the same stress in neighbouring grains, having different elastic constants, must produce different strains these grains).

As was proved by Hill the Voigt and Reuss averages can be considered only as an upper and lower bounds of the true elastic coefficients of the multiphase or polycrystalline material. He proposed the arithmetic average of these two averages as a more reliable estimate of elastic coefficients of real materials. The Hill average, in spite of its simplicity, proved to be well justified by many more sophisticated theoretical models giving tighter bounds for effective elastic constants (Hashin–Shtrikman [8], Kröner [9]).

For these reasons it is assumed that the Hill average is the best theoretical estimate of effective elastic constants of considered composite materials. The Hill stiffness matrix has the same symmetry and form as the discussed earlier Voigt and Reuss stiffness matrixes. Its components are given by:

$$c_{11}^{kH} = \frac{1}{2}\left(c_{11}^{kV} + c_{11}^{kR}\right),$$

$$c_{33}^{kH} = \frac{1}{2}\left(c_{33}^{kV} + c_{33}^{kR}\right),$$

$$c_{44}^{kH} = \frac{1}{2}\left(c_{44}^{kV} + c_{44}^{kR}\right), \qquad (4.23)$$

$$c_{12}^{kH} = \frac{1}{2}\left(c_{12}^{kV} + c_{12}^{kR}\right),$$

$$c_{13}^{kH} = \frac{1}{2}\left(c_{13}^{kV} + c_{13}^{kR}\right).$$

5. Discussion and experimental verification

The effective elastic moduli of composite material can be numerically calculated by successive use of expressions (4.16), (4.21), (4.22) and (4.23). They will depend on the stiffness moduli and volume fractions of the two composite components, i.e. superhard phase and binder-catalyst phase. Moreover,

in contrast to the previously proposed models, they will also depend on the texture of superhard phase described by the W_{400} expansion coefficient of ODF function.

The elastic coefficients of typical components of superhard materials (diamond, cBN, Co, TiN, AlN, Ti3SiC2) can be found in the literature [3, 7, 13]. The moduli used in the subsequent example calculations are listed in Table 1.

TABLE 1. The stiffness coefficients of typical components of superhard composite materials.

Material	C_{11} [GPa]	C_{12} [GPa]	C_{44} [GPa]	Type
cubic BN	820	190	480	single-crystal
Co	267	–	72	isotropic
AlN	334	–	130	isotropic
TiN	532	–	190	isotropic

The stiffness coefficients for the cubic boron nitride (the superhard phase) are similar to those for single crystals whereas the coefficients of binder-catalyst phases are similar to those of isotropic media. It reflects the fact that in the model directional averaging is performed only for superhard phase assuming binder phase isotropic.

Resultant anisotropy of composite material is fully described by the texture coefficient W_{400} of the superhard phase. As was already noticed in earlier papers anisotropic properties of these kind of materials were disregarded. Up to our knowledge there is no experimental data on texture parameters of superhard composites. Such data could be obtained for example from X-ray or neutron diffraction experiments.

Despite for the lack of such data for the time being it is still possible to make some estimation of elastic constants assuming different possible values of W_{400}. To this end we can define three specific, border line, cases of the orientation distribution function ODF:

(a) fully isotropic with a uniform distribution of crystallites orientations in all directions, i.e. $W_{400} = 0$,

(b) transversally isotropic with all crystallites oriented with [1,0,0] crystallographic direction parallel to the sample technological axes, i.e. $W_{400} = 0.03134$,

(c) transversally isotropic with all crystallites oriented with [1,1,1] crystallographic direction parallel to the sample technological axes, i.e. $W_{400} = -0.02089$.

Considering (b) and (c) as border line cases we can expect in real composites the values of texture parameter W_{400} in the range from -0.02089 to 0.03134. We will examine now how the value of texture parameter influences the effective elastic moduli of composite. Because in many technical papers the elastic properties of materials are expressed in terms of the Young modulus E and Poisson ratio ν we will express our results in the same way. The formula for the elastic moduli on the basis of effective stiffness coefficients are given by:

$$E_z = \frac{c_{33}^{kH}(c_{11}^{kH} + c_{12}^{kH}) - 2(c_{13}^{kH})^2}{(c_{11}^{kH} + c_{12}^{kH})},$$

$$\nu_z = \frac{c_{13}^{kH}}{c_{11}^{kH} + c_{12}^{kH}},$$

(5.1)

where E_z and ν_z are the moduli in the z-direction.

The dependence of the effective Young modulus and Poisson ratio on the texture coefficient W_{400} for typical composition of superhard material (80% cBN + 20% AlN) is illustrated in Fig. 2 with a solid lines.

It can be seen that texture of superhard phase may significantly change the Young modulus and Poisson ratio of the composite material as compared to the isotropic case. In the considered example the Young modulus can deviate up to 15% from its isotropic value and Poison ratio even more.

It is clear that texture of superhard phase is an important factor influencing macroscopic elastic properties of composites.

Another important conclusion which can be drawn from the presented model concerns ultrasonic measurements of elastic moduli of composite materials. In such measurements velocities of shear and longitudinal ultrasonic waves are measured in axial direction of disc shaped composite samples. Then, the elastic moduli of the material are derived on the bases of measured velocities and density. If at these point we make unjustified assumption that the material is isotropic and use for calculation of elastic moduli the standard "isotropic" formula we will obtain results considerably different from the right values. The extent of this problem is illustrated in Fig. 2, where such apparent ultrasonic moduli are shown in comparison with the right ones. The non-conformance is especially pronounced in estimation of the Poisson ratio where for highly [1,0,0] textured cBN phase we obtain negative values of this ratio.

To get reliable estimation of elastic moduli from measurements of ultrasonic velocities in one direction it is necessary to ensure that the material is truly isotropic. In the case of substantial anisotropy the measurement procedure must be considerably modified by using additional propagation di-
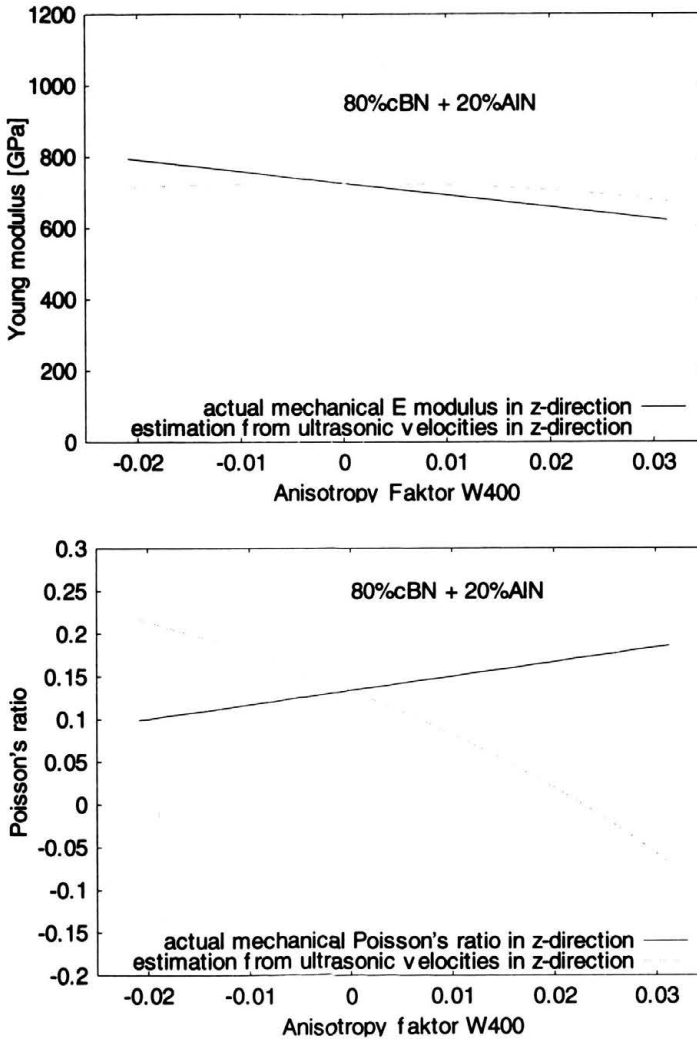
FIGURE 2. Dependence of Young modulus and Poison ratio on the texture coefficient W_{400} for typical composition of superhard material.

rections and more sophisticated calculation algorithm. Moreover, in such a case the description of elastic properties of composite material should be expressed rather in terms of stiffness coefficients than the Young modulus and Poison ratio.

To make full experimental verification of the proposed model it is necessary to compare theoretical results with the experimental elastic coefficients determined on the samples with controlled anisotropy. Unfortunately, in all available experimental papers on elastic properties of superhard composites

the authors assumed isotropic condition without any evidence of experimental verification. It means that their data may be subject to errors in case the tested materials were not truly isotropic.

Nevertheless in Fig. 3 we present the available experimental data on the Young modulus of different grades of cBN composites [2] together with theoretical estimations calculated from the proposed model. The materials have different contents of superhard phase (from 65 to 97 vol % of cBN) and different kinds of binder-catalyst phases (TiN, AlN, Co). Because of lack of data on the actual texture of measured samples in theoretical calculation, we assumed perfect isotropy ($W_{400} = 0$).
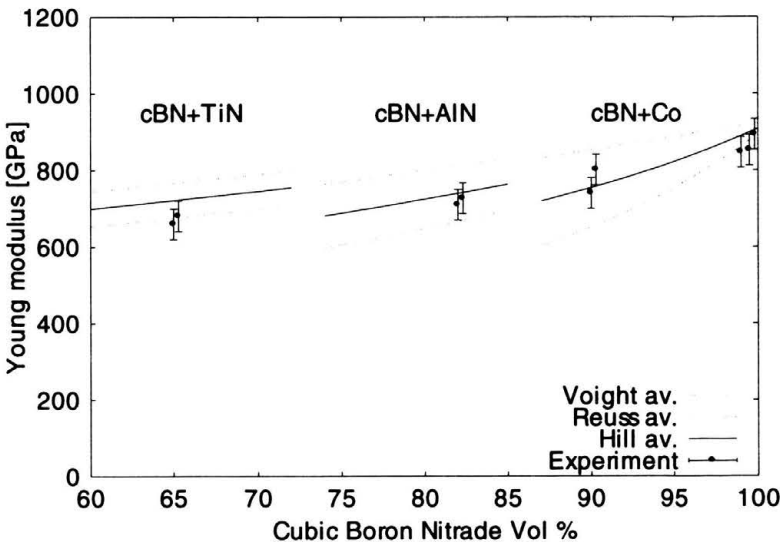

FIGURE 3. Comparison of theoretical and experimental values of Young modulus for different grades of superhard composite based on cubic boron nitride.

In spite of this simplifying assumption (adopted both in the elaboration of experimental data and in theoretical model) the agreement is reasonably good. The measured values of the Young modulus are generally slightly below the calculated Hill averages. The main reasons for observed discrepancies, except the simplifying assumption of isotropy, are uncertainties concerning actual phase composition of modelled materials and actual values of elastic moduli of binder-catalyst phase. The mentioned uncertainties are consequence of the fact that during high-pressure, high-temperature composite synthesis initial components can react making different additional compounds and/or solid solutions.

6. Conclusions

The theoretical model was proposed for calculation of the effective elastic moduli of superhard composites on the basis of polycrystalline diamond (PCD) and cubic boron nitride (cBN). We use simple Voigt, Reuss and Hill averaging procedures over orientation distribution of crystallites and volumes of component phases.

Our approach, as compared to the previous ones, takes into account the texture of superhard phase. The texture of composite material can be a consequence of anisotropic synthesis condition in the high-pressure chambers.

The model shows reasonably good agreement with experimental data obtained on commercial grades of CBN composites but for full verification of its accuracy it is necessary to have experimental data on elastic moduli together with data on texture of superhard phase. Experimental works in these direction are planned.

The elastic moduli calculated from the model can serve as reference values for the elastic moduli measured on fabricated composite samples. Combined with ultrasonic measurement techniques it can give a valuable tool for evaluation of new grades of composite materials. Such reference values can also be useful in non-destructive quality control in production process.

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