

Identification of Coefficients of Thermal Expansion of Pyrolytic Carbon with Different Texture Degrees

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Abstract. Carbon/carbon composites fabricated by chemical vapor infiltration (CVI) consisting of carbon fibers in a pyrolytic carbon matrix are particularly interesting for industrial application due to their high strength and light weight. The pyrolytic carbon shows four forms with a different polycrystalline structure: isotropic, low textured, medium textured and high textured [1]. The effective compliance and elasticity tensors were theoretically identified with a help of homogenization [2]. This paper discusses a method for calculation of effective coefficients of thermal expansion for different structural modifications of pyrolytic carbon. In essence, we model the pyrolytic carbon as a system of single graphite crystals with stochastically distributed orientations (spatial angular positions) embedded in an infinite homogeneous matrix. For description of spatial angular positions in a graphite pattern we utilise normal probability density function, which were experimentally identified in [1]. The effective coefficient of thermal expansion were calculated with a help of homogenisation method. The obtained results were compared with experimental and theoretical data [3-5].

Introduction

The prediction of the coefficients of thermal expansion of carbon/carbon composites fabricated by chemical vapor infiltration (CVI) is important for their effective industrial applications. These composites consist of carbon fibers embedded in a matrix of pyrolytic carbon. The pyrolytic carbon matrix around the fibers has a cylindrically layered structure and each layer may have different coefficients of thermal expansion in the axial, radial and circumferential directions, i.e., it is anisotropic. The number of layers, their width, order and structure are influenced by the deposition parameters. The material of each layer is a pyrolytic carbon, which exhibits a broad variety of microstructures. On the basis of four different types of preferred orientation (or texture) there are four basic forms of pyrolytic carbon: isotropic (ISO), low- (LT), medium- (MT) and high-textured (HT) [1]. Some experimental and theoretical investigations leading to the determination of coefficients of thermal expansion of pyrolytic carbon and pyrolytic graphite are published in [3-5], but all these investigations were performed for pyrolytic carbon without significant modifications of this material. The differences between the coefficients of thermal expansion for different modifications of pyrolytic carbon is very significant and knowledge of their values is very important for investigations of damage processes in carbon/carbon composites.

Material description

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Theoretical investigations of heterogeneous materials and structures aim to derive the effective elastic properties, with respect to imposed loading, known distribution of the material parameters, geometry and characteristic material length scales. The so called *representative volume element* (RVE), a suitably large sample which is a good representative of the material microstructure, was defined in [6] and elsewhere. In real heterogeneous materials the dimensions of the RVE on the smaller level of the characteristic length l are typically very small in comparison with the dimensions on the length scale L of the higher level. The ratio of these smaller and larger scales $k = l/L \ll 1$ is represented by a very small positive number.

The basic idea for the elaboration of the modeling of the pyrolytic carbon material is to utilize the real physical 2D spatial distribution of carbon structural units obtained directly from experimental methods. For this purpose, first the experimental values of texture degrees (in the surface perpendicular to the fiber axis), extracted by selected area electron diffraction (SAED) [1,7] have been used as reference points for the modeling of spatial distribution functions. The full width at half maximum along the azimuthal intensity distribution of the ring-shaped (00 l) reflections of SAED patterns (Fig.1a) is used to quantify the texture degree of carbon planes in relation to the fiber surface and is denoted as orientation angle (OA) (Fig. 1b).

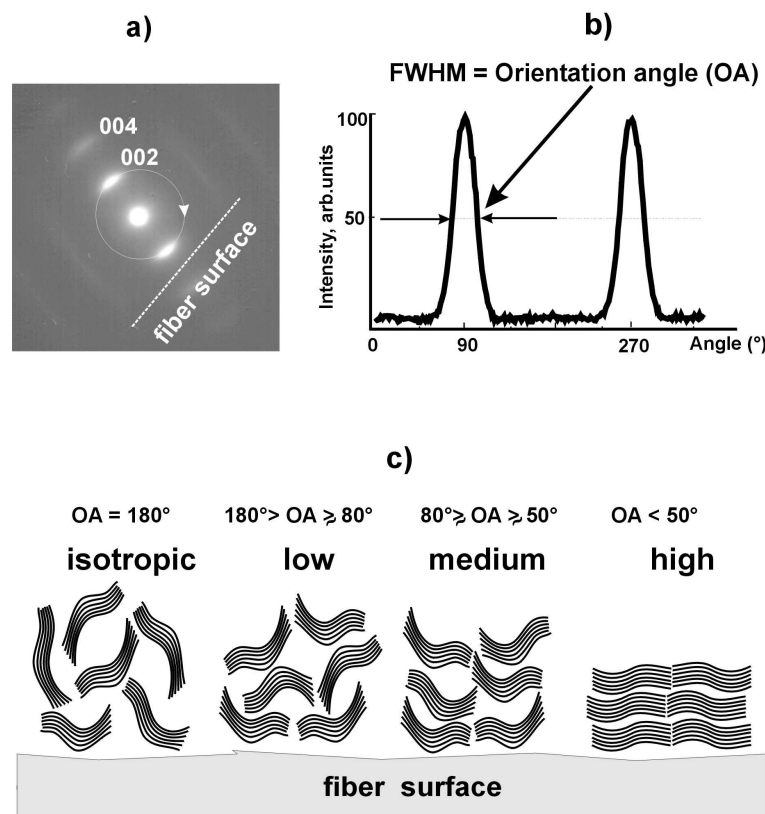


Fig. 1. Determination of the degree of texture in the surface perpendicular to the fiber axis of pyrolytic carbon material. a) SAED pattern with the white overlaid circle showing the direction of the azimuthal intensity scan; b) the extracted azimuthal intensity scan; c) a semi- quantitative correlation between texture types and OA values [1].

Orientation angles from $<180^\circ$ to 80° , 80° to 50° and $< 50^\circ$ corresponding to LT-, MT- and HT-carbon, respectively (Fig. 1c) [1]. The experimentally determined curves was fitted using different

kinds of statistical distribution functions using Origin® software. The best fitting corresponds to the Gaussian density function: $f(\beta) = (\sigma\sqrt{2\pi})^{-1} \exp(-\beta^2/2\sigma)$, where β - describes the angle of the crystal orientation, and $\sigma = OA/2$. Fig. 2 shows the representative Gaussian density distribution functions for different modifications of the pyrolytic carbon: LT - $0.7 \leq \sigma \leq \pi/2$; MT - $0.44 \leq \sigma \leq 0.7$ and HT - $\sigma \leq 0.44$.

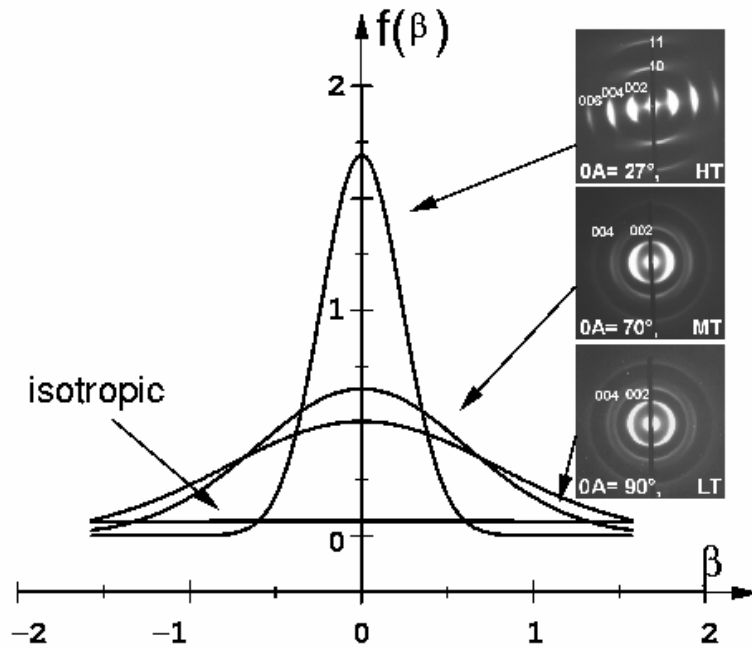


Fig.2. Typical Gaussian density distribution functions and SAED patterns of differently textured pyrolytic carbon matrix layers [2].

The selection of the RVE was based on considering the ratio of diameter of the analyzed area, i.e. the diameter of SAED aperture (characteristic length L) to the average size of the coherent domains (characteristic length l) extracted from HRTEM-images. In our case the diameter of SAED aperture was about 2 μm , i.e. a relatively large specimen was analyzed. The average value of coherent domain was taken as 15 nm [7]. The corresponding coefficient k is about $7.5 \cdot 10^{-3}$, i.e. it fulfils the selection of RVE [6].

Material modeling

The RVE can be regarded as a polycrystal. Each single crystal of this polycrystal may be treated as an inclusion embedded in the remaining crystals. In this case there is complete symmetry in treating each crystal as the inclusion [6]. On this basis the polycrystalline pyrolytic carbon material is modeled as a system of single graphite crystals (SGCs) embedded in an infinite homogeneous matrix with unknown effective (overall) coefficients of thermal expansion (Fig. 3).

Each SGC is characterized by an angle β_i between the transversal isotropy axis Z^{β_i} of the crystal of graphite (in the local coordinate system of the crystal) and Z in the global coordinate system. The coefficients of thermal expansion α_{ij} are the components of a second order tensor; they can be

calculated in the global coordinate axis orientation (X, Y, Z) using their known values in the local coordinate axis orientation $(X^{\beta_i}, Y^{\beta_i}, Z^{\beta_i})$, see Fig. 3.

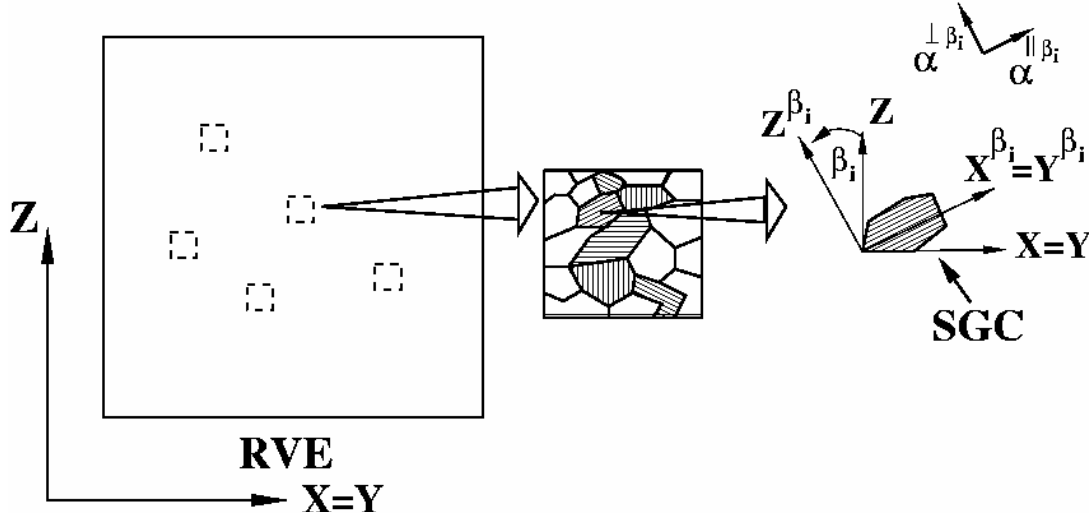


Fig.3. The RVE: the system of SGCs with different orientations β_i to the global coordinate system (X, Y, Z) .

Then the tensor of thermal expansion of the crystal of graphite in the global coordinate system is:

$$\alpha^{\beta_i} = Q^{\beta_i T} \alpha Q^{\beta_i}, \quad (1)$$

where Q^{β_i} is a transformation matrix for the crystals with orientation angle β_i and the coefficients of thermal expansion α (components $\alpha_{ii} = \alpha^{\perp}, \alpha^{\parallel}$) of graphite in the local coordinate system. The graphite is orthotropic and the X, Y and Z axes are in the planes of symmetry, the thermal shearing coefficients are zero: $\alpha_{ij} = 0$ for $i \neq j$. In this case (1):

$$\alpha^{\perp \beta_i} = \alpha^{\perp} \cos^2 \beta_i + \alpha^{\parallel} \sin^2 \beta_i, \quad \alpha^{\parallel \beta_i} = \alpha^{\perp} \sin^2 \beta_i + \alpha^{\parallel} \cos^2 \beta_i. \quad (2)$$

In the literature different methods for the theoretical calculation of coefficients of thermal expansion are proposed [8-11]. The effective coefficients of thermal expansion can be calculated as the averaged value of all aggregates of the crystals. As a basis of this calculations a well known simple method, the so-called rule of mixtures [11], is used. The unknown values of α for discrete crystal distributions (with n different crystal orientations) can be calculated as:

$$\hat{\alpha} = \sum_{\beta_i}^n f^{\beta_i} \alpha^{\beta_i}, \quad (3)$$

where f^{β_i} is the volume fraction of crystals with orientation angle β_i . The continuous distribution of crystal orientations for each type of texture is experimentally derived as a Gaussian distribution function $f(\beta)$. Then the effective coefficients of thermal expansion (3) in the global coordinate system can be calculated as the limit with $\Delta\beta_i = \beta_i - \beta_{i-1} \rightarrow 0$:

$$\hat{\alpha}^{\perp} = \lim_{\Delta\beta_i \rightarrow 0} \sum_{\beta_i} f^{\beta_i} \alpha^{\perp \beta_i} = \alpha^{\perp} \int_{\beta} f(\beta) \cos^2 \beta d\beta + \alpha^{\parallel} \int_{\beta} f(\beta) \sin^2 \beta d\beta,$$

$$\hat{\alpha}^{\parallel} = \lim_{\Delta\beta_i \rightarrow 0} \sum_{\beta_i} f^{\beta_i} \alpha^{\parallel \beta_i} = \alpha^{\perp} \int_{\beta} f(\beta) \sin^2 \beta d\beta + \alpha^{\parallel} \int_{\beta} f(\beta) \cos^2 \beta d\beta.$$

Numerical results

The coefficients of thermal expansion $\hat{\alpha}^{\perp}$ and $\hat{\alpha}^{\parallel}$ as functions of texture degree are presented in Fig. 4.

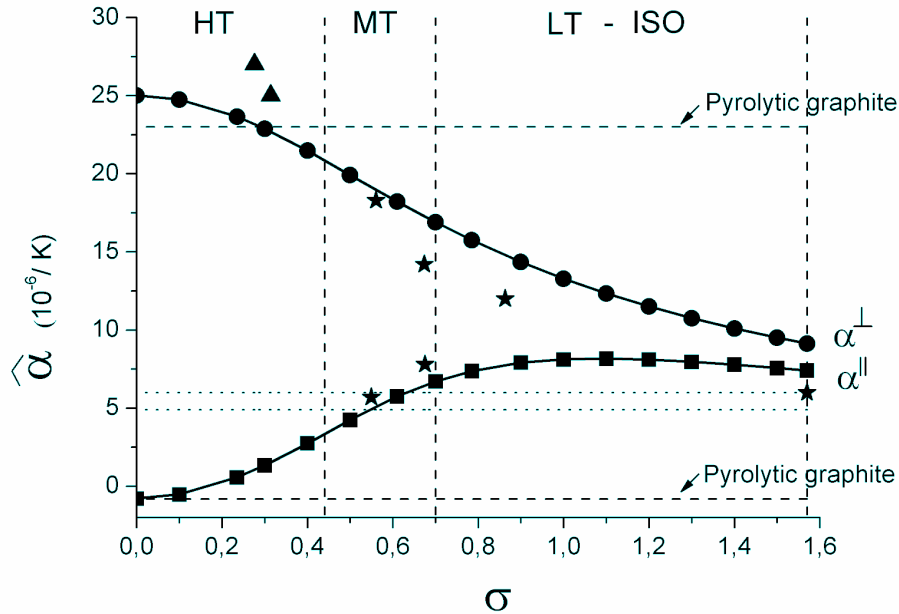


Fig. 4. Coefficients of thermal expansion $\hat{\alpha}^{\perp}$ and $\hat{\alpha}^{\parallel}$ as a functions of σ and experimental and theoretical results from the literature [3-5].

The coefficient $\hat{\alpha}^{\perp}$ for HT carbon is very high in comparison to $\hat{\alpha}^{\parallel}$. It also follows from experimental data [4] for pyrolytic graphite (dashed lines and triangular symbols in Fig. 4). For the MT modification, this difference is smaller and for LT carbon this difference is small. This results were compared with theoretical and experimental data [3] (star symbols in Fig. 4). For $\sigma \rightarrow \pi/2$, the coefficients of thermal expansion tend to the coefficients of thermal expansion of an isotropic material. In this case $\alpha^{\perp} \approx \alpha^{\parallel}$ is approximately $6-8 \times 10^{-6} K^{-1}$, and resulting from experiments it is in the range $4-6 \times 10^{-6} K^{-1}$ [3]. Experimental and theoretical data [5] are smaller like in our case (dotted lines in Fig. 4). The reason is given in [3]: it has been investigated for composites in which the fibers lie preferentially in the xy planes but are random in directions within those planes. Along the x -axis (or the equivalent y -axis) of the sample the directions of the fibers are random and therefore the contribution of the higher radial expansion (in our case $\hat{\alpha}^{\perp}$) is limited.

Conclusions

The bases of our investigation was the assumption that the material of coherent domains is graphite without defects and the turbostratic character of graphene layers in pyrolytic carbon as well as other types of defects were neglected. However, for the present investigations this assumption is useful

for regarding the correlations between the texture degree and the coefficients of thermal expansion of pyrolytic carbon matrices.

The main results of this study are:

- 1) This work is a first implementation of a simple homogenization method for modeling the influence of microstructure on the coefficients of thermal expansion for pyrolytic carbon with different texture degrees.
- 2) The experimental data from the real physical structure obtained by SAED and HRTEM is used as input data for identification of the 2D spatial distribution of carbon structural units of the modeling.
- 3) Basis of this model calculation have been made for the coefficients of thermal expansion as functions of the texture degree of polycrystalline pyrolytic carbon material. These theoretical results are consistent with results obtained experimentally for carbon/carbon composites.

Acknowledgments

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