QUANTITATIVE DETERMINATION OF THE MISORIENTATION DEGREE OF PYROCARBONS

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Abstract

The orientation angle (OA), corresponding to the full-width at the half maximum (FWHM) intensity of the opening angle of the arc of (002) reflections, displays an important role for the quantitative evaluation of pyrocarbon textures. In this study, a quantitative method for determining the misorientation degree of pyrocarbons was proposed based on the high resolution transmission electron microscopy (HRTEM) and the selected area electron diffraction (SAED) by the computer-aided image analysis. Fast Fourier transform (FFT) of the HRTEM image was performed to obtain the diffractogram of the pyrocarbon layers in the reciprocal space. The gray centroid method and the scanning algorithm with a polar axis were applied to extract the azimuthal intensity maxima of the ring (002) reflections. OA was obtained by an improved Gaussian function with a direct component fitting the intensity data versus the azimuth angle. The FFT can be avoided when measuring OA from the SAED pattern. The accuracy of the algorithm has been approved by measuring the SAED images in some research work reported by others. The system has been applied to the quantitative texture characterization of pyrocarbon matrix of carbon/carbon composites fabricated by CVI, and the misorientation degree has been appraised at a higher precision compared to the polarized light microscopy (PLM).

Keywords: pyrocarbon; misorientation degree; orientation angle; transmission electron microscopy; image analysis.

Introduction

Pyrolytic carbon, a matrix component of carbon/carbon (C/C) composites fabricated by the chemical vapor infiltration (CVI), exhibits a broad variety of microstructures, ranging continuously from the near amorphous to the highly crystalline graphitic state. It has been known that the physical properties and mechanical behavior of the composites depend strongly on the matrix microstructure. The CVI process has been used to fabricate C/C composites for a long time, but it is still difficult to obtain carbon matrices with well-defined micro- and nanostructural properties owing to complicated infiltration conditions. Therefore, the precise characterization of microstructure variation of the deposited carbon is a primary precondition to realize the objective control of the carbon structure and to scientifically understand the correlation between the texture formation and the chemistry and kinetics of CVI.

Polarized light microscopy (PLM) is frequently employed to determine the texture. The optical anisotropy of different pyrocarbon can be qualitatively described by apparent morphology in PLM. For the quantitatively characterizing the various microstructures of pyrolytic carbon, the extinction angle (Ae) was introduced as a classified criterion: isotropic pyrocarbon (ISO, Ae<4°), dark laminar (DL, 4°<Ae<12°), smooth laminar (SL, 12°<Ae<18°), and (RL, Ae>18°). Nevertheless, the applicability of Ae is still unsatisfactory except for pyrolytic carbon circularly deposited around rotational symmetry substrates such as carbon fibers, spherical (fuel) particles, or capillary walls. Additionally, the resolution in PLM is restricted by the wavelength of visible light, and submicron structures like fiber–matrix inter-phases existing in C/C composites or so-called ISO carbon with a weakly light reflectance cannot be analyzed.

High-resolution transmission electron microscopy (HRTEM) is a powerful complementary technique, since it provides valuable data for an analysis of all kinds of pyrolytic carbon at a nanometer scale. The misorientation of

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carbon layers also is assessed by orientation angle (OA) measured from the selected area electronic diffraction (SAED), introduced by Bourrat et al. OA, corresponding to the full width at half maximum (FWHM) intensity of the azimuthal opening of the arc of (002) reflections, is a quantitative and clear criterion of the degree of preferred orientation. Therefore, the texture characterization at a significantly higher spatial resolution compared with PLM can be performed by measuring the OA from TEM selected area electron diffraction patterns. The pyrolytic carbon textures are defined according to their degree of preferred orientation around the basal planes as isotropic (ISO, OA=180°), low textured (LT, 180°<OA≤80°), medium-textured (MT, 80°<OA≤50°) and high-textured (HT, OA<50°) carbon. The preferred orientation with OA and Ae is about linearly related. But the degree of preferred orientation characterized by OA is a more sensitive and precise technique to quantify adequately the anisotropy of the matrix compared with that by Ae.

Though OA has been regarded as an important role for the quantitative evaluation of pyrocarbon textures, the detailed study about how to determine OA value was little reported. Tressaud et al. adopted the larger value of the FWHM peak of fast Fourier transform (FFT) corresponding to the HRTEM image of F-intercalated fibers to accounts for the departure from parallelism of the graphene layers. Bourrat et al. proposed that OA was obtained by fitting the azimuthal intensity along Debye-Scherrer ring in SAED patterns to the Gauss curves. But the detailed description about the measurement procedure had been neglected in their papers. In the subsequent studies, the measurement of OAs mentioned has only been explained by citing Tressaud's or Bourrat's method. In this study, a technique of computer-aided image analyses is described and implemented for the quantification of the preferred orientation by determining OA of pyrocarbons. HRTEM images and SAED patterns of pyrocarbons with various microstructures fabricated by ICVI are considered for the present study. Some precise and practicable techniques of image processing are adopted to establish a measurement system with human-computer interaction. With the aid of this work, the misorientation degree of carbon layers can be assessed so that the mechanical properties should be predicted and the growth mechanism of pyrocarbons under various deposition conditions be analyzed.

Measurement algorithms

HRTEM is a conventional characterization technique, revealing the misorientation degree of aromatic layers corresponding to the based plane. Orientation angle (OA) determined from HRTEM images requires several steps consisting of image analyses, data collection and nonlinear fitting.

Image analyses

A TEM lattice-fringe image given in Fig.1a is obtained from C/C composites fabricated by ICVI. Fast Fourier transform (FFT) of the image is performed shown as Fig.1b. FFT images are equivalent to SAED patterns, imaged in the reciprocal space, of the analog picture. Therefore, the anisotropy of various pyrocarbons can be evaluated through the analysis of the FFT image, reflecting the predominant spatial frequency, as well as the SAED pattern. The FFT image visualizes zero-frequency component in the middle of the spectrum array with the same size as the original HRTEM. Considering computational efficiency, the square matrix only including diffractogram information centering the zero-frequency is required by truncating the parts away from the 002 arcs. An average filter is used to eliminate high-frequency and low-frequency noises, giving rise to the better result compared with that of other filters (e. g., medium filter, wiener filter or laplacian). The diffractogram information in the FFT is distinguished by adjusting image intensity with linear mapping shown in Fig. 1c. It can be seen that the FFT is much similar to the corresponding SAED pattern presented in Fig. 1d. Thus, the mapping image of 002 lattice-fringes in the reciprocal space can act as a media for the quantitative characterization of disorientation of aromatic layers.

Data sampling

The intensity data along the circumference of ringed 002 arcs are extracted by scanning with a rotating polar axis Op showed in Fig. 2a. The origin O must be first fixed. Since the zero-frequency point is the center of the preprocessed FFT image with diffraction symmetry, a so-called centroid algorithm with weights of grayscale is improved to locate the center point of the FFT automatically. The location precision of image is up to subpixel level by the method.

The gray barycentric coordinate ($x0$, $y0$) in the FFT image is expressed as follows,

$$x_0 = \frac{\sum_{i,j} iI(i,j)}{\sum_{i,j} I(i,j)} \quad (1)$$

$$y_0 = \frac{\sum_{i,j} jI(i,j)}{\sum_{i,j} I(i,j)} \quad (2)$$

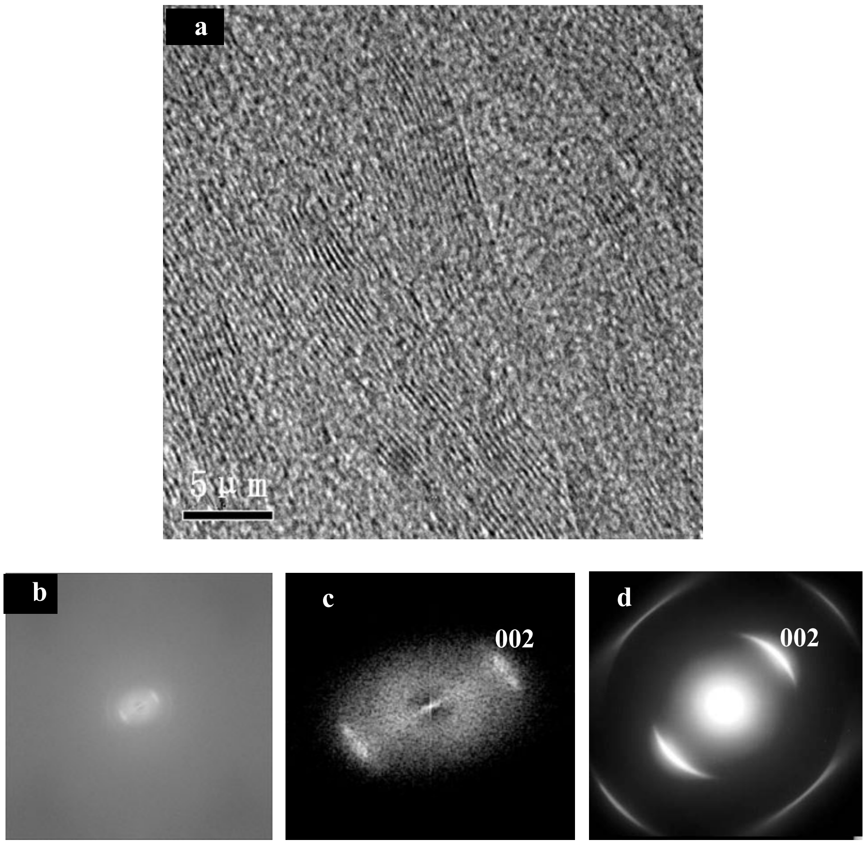


Figure 1. TEM lattice-fringe image in (a) and comparison between FFT image (b, c) and SAED pattern (d).

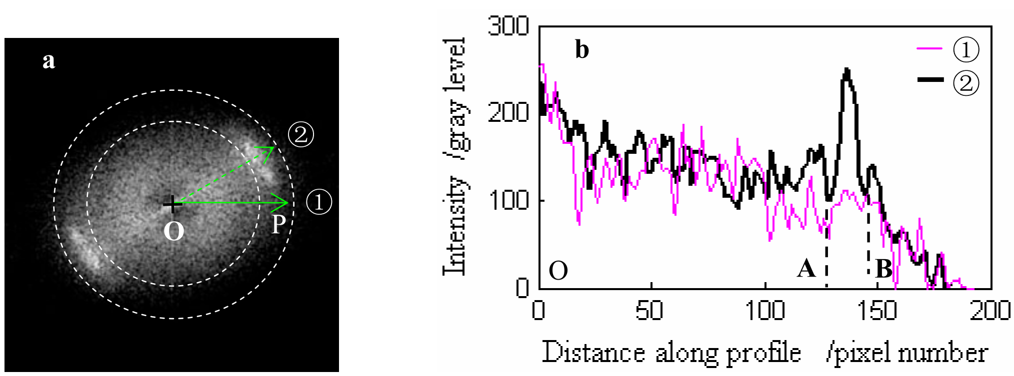


Figure 2. Image analysis procedure of sampling intensity data based on the FFT image. Schematic diagram of polar axis scanning with the origin of gray barycenter shown in (a) and intensity profile along the polar axis directions in (b). The legends correspond each other.

where I(i, j) denotes the gray level of the pixel at the ith row and the jth column. The black intersection point in Fig. 2a is the computed origin marked by O.

The ringed scope, from which the intensities of 002 reflection will be extracted, requires plotting out. OP, as a polar axis, rotates round the fixed origin O located by the gray centroid method, and information about the variety of gray levels along the different OP direction can be detected. The intensity profiles, □ and □ in Fig. 2b, respectively correspond to the intensity distribution at the two representative OP orientation of the FFT image shown in Fig. 2a. The profile □ is gained when OP is just passing across 002 arcs. The maximum peak of the profile □, excepting the area around the origin, occurs at the predominant spatial frequency. The two turning points away from the maximum are signed as A and B. The ringed zone between the two concentric circles respectively with the radius OA and OB is considered as the scope for sampling the intensity data like as shown in Fig. 2a.

The azimuthal intensity data are obtained by scanning along the circumference of the well-defined loop. The polar axis OP is again turning around on the center O from a starting location without predominant peak of its intensity profile. The maximum of gray scale within the ringed zone along each OP orientation is collected for the determination of orientation angle (OA). The sampling is performed with OP rotating from 0° to 360° at intervals of 3°.

Data fitting

The intensity data from the ringed-shape (002) reflections versus azimuth angles are fitted using Gaussian function by least squares criterion. Gaussian distribution formula is commonly expressed as follows:

$$y(x) = A\exp\left(-\frac{2(x-x_0)^2}{\omega^2}\right) \quad (3)$$

where A denotes the “amplitude”; the center x0 presents the “mean”; while ω/2 is the standard deviation. The intensity, y, is a variable depending on the independent azimuth angle, x. A constant component y0 is added to the function considering the intensity related to gray scale in the FFT image. There are the two ways to fit the data.

After all active data (x, y) is averagely divided into two groups, (x1, y1) and (x2, y2), the two curve of single Gaussian peak is respectively fitted to them. So, Gaussian expression is written as:

$$y(x) = y_0 + A\exp\left(-\frac{2(x-x_0)^2}{\omega^2}\right) \quad (4)$$

(2) A curve with double Gaussian peaks is applied to fit all active data. Then, Gaussian function is expressed as:

$$y(x) = y_0 + A\exp\left(-\frac{2(x-x_{01})^2}{\omega^2}\right) + A\exp\left(-\frac{2(x-x_{02})^2}{\omega^2}\right) \quad (5)$$

Gaussian fit is repeated within 95% confidence interval several times for the improvement of fitting precision. The sampling points with higher residual errors, the differences between the theoretical Gaussian function and the actual data points, will be eliminated about 5％ after Gaussian fitting is performed every time.

ω of all Gaussian parameters is especially concerned owing to the relation with orientation angle (OA). There is such a functional expression between ω and OA:

$$OA = \sqrt{2\ln 2}\,\omega \quad (6)$$

Here, ω is the average of the results from the two algorithms.

Results and discussion

Pyrocarbon with different textures and interlayers is often studied by HRTEM on a submicron- and nanometer scale. Orientation angle (OA) has been commonly received as the precise characterization parameter for the evaluation of carbon textures. It is significant to study the measurement of determining OA from HRTEM. OA is defined as the full width at half maximum (FWHM) intensity of the azimuthal opening of the arc of (002) reflections based on the SAED pattern. It quantifies the local structural anisotropy by measuring the layer’s disorientation deviating from the based plane. The FFT of the HRTEM picture is equivalent to the SAED pattern imaged on the reciprocal space. OA from FFT images is also an equivalence relation with OA from SAED. Thus, the algorithm is similarly applicable to SAED patterns.

In fact, there are always some distances along the opening interval of the predominant frequency ring in FFT images or of the 002 arcs in SAED patterns especially for high textural pyrocabon, so that the start orientation for scanning intensity data isn't always the direction of symmetry axis of the Debye-Scherrer ring. Most of the azimuthal distribution of the extracted intensity data appears in asymmetry, which has an impact on the fitting precision. Therefore, the function of adjusting azimuthal order is affiliated with the measurement for a guarantee of the symmetrical intensity data.

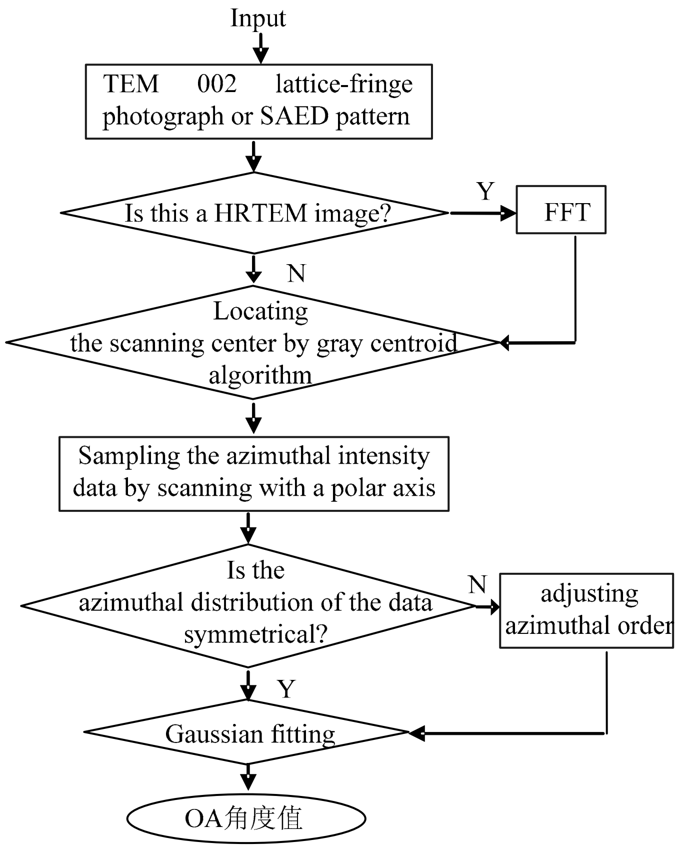


Figure 3. Schematic diagram of measuring OA

The schematic representation about the measurement of OA is shown in Fig. 3. The step of FFT can be skipped over if a SAED pattern is inputting. Therefore, the anisotropy of various pyrocarbons can be assessed through the analysis of HRTEM image as well as SAED patterns using the procedure in Fig.3. The 002-lattice fringe and the SAED pattern presented in Fig.1a and 1d are given an example to test the validity of the measurement. The diffractogram of the 002-lattice fringe is first obtained by FFT. Then, the gray centroid algorithm is performed to locate the origin of scanning the Debye-Scherrer ring. The gray centroid is perfectly precise for FFT images, while the centroid point of SAED patterns is likely to departure from their geometrical center owing to the negative dissymmetrical. Though a little offset doesn't impact on sampling intensity data, in advance cutting the digital image of SAED pattern as symmetrical as possible is required so that the procedure is successfully going. The extracted intensity by the polar axis scanning and the Gauss curves are illustrated versus azimuthal angles in Fig. 4. It can be seen from Fig. 4a and 4c, which respectively correspond to the FFT (Fig. 1c) of the HRTEM image (Fig. 1a) and the SAED pattern (Fig. 1d), that the original azimuth intensity is distributed in asymmetry. The results from three different Gaussian fits, after adjusting the sequence of the azimuth intensity and eliminating the data with higher residual errors, are given in Fig. 4b and 4d. The OA of the HRTEM presented in Fig. 1a is computed to 46° and the OA of the SAED pattern in the Fig.1d is 42° by averaging the numerical values from the three fitting methods. According to the received terminology, they belong to the high-textured pyrocarbon.

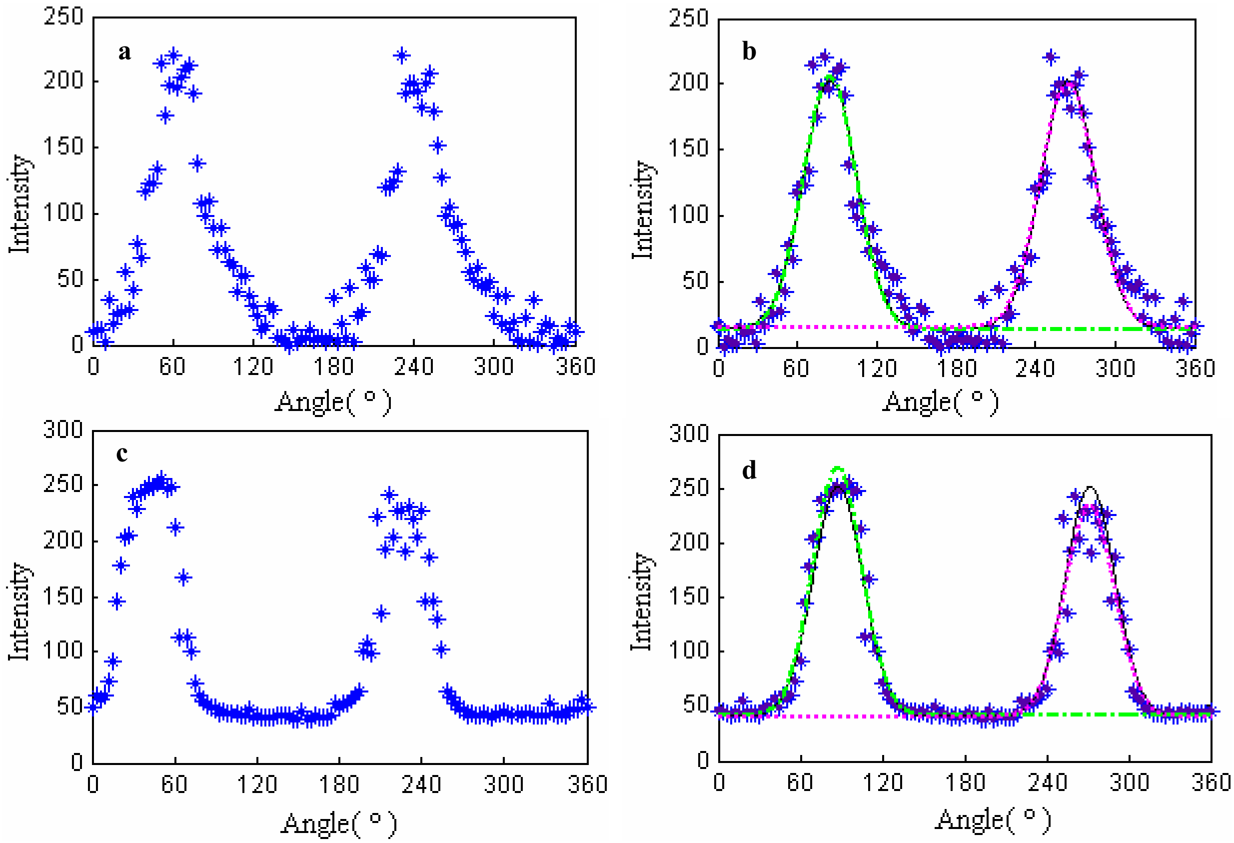


Figure 4. Data analysis procedure of measuring the orientation angle (OA) based on the HRTEM images or SAED patterns. The scatter diagrams of azimuthal intensity through scanning the arc of (002) reflections of Fig.1c and Fig.1d are given in (a) and (c). The Gauss curves, (b) and (d), fit the adjusted data correspond to (a) and (c). Green dash-dot line (**-.**) and magenta dotted line (:) respectively denote the Gauss curve with a single peak fitting to the two grouped data.; black solid line expresses the function with double Gaussian peaks fitting to all data.

The system is repeatedly modified by testing orientation angles of pyrocarbons with different texture variety for improving its adaptability. It is the key problem how to set the initialization of Gauss parameters optimized by iterative algorithm with least square errors especially when low-textured or isotropic carbons are analyzed. There is no question about “mean”, x0, equal to 90° or 270°. The minimum of the sampled data is presumed as the constant component, y0, while the difference between the maximum and the minimum is the pre-given amplitude, A. But ω, which is equal to 2σ, the standard deviation within 95% confidence interval, requires taking deliberate action because OA is correlated with it according to the expression (6). If OA=180°, ω180≈153°. The azimuthal intensity for the absolute ISO carbon should be linear in theory owing to its ringed 002 arcs close. Gaussian function fits to a line without iteration, so the initial parameters are keeping. Therefore, the initialization of ω is considered as ω180 to make an agreement between the result from the measurement and the physical meaning of OA. Such an initialization not only decreases iteratively computing times but also ensures the measurement sensitivity for the various textures of pyrocarbons.

The procedure is used to assess the multilayer textures of C/C composite by ICVI. The carbon fibers are surrounded by three pyrolytic carbon layers numbered 1 to 3 with different degrees of textures in PLM presented as Fig. 5a. The extinction angles (Ae) of the 2nd and 3rd layer have been obtained by the classical measurement in PLM with the eyes or by the analysis the sequential images along with the analyzer rotating.But the first layer is hardly identified in PLM owing to slightly optically anisotropic if any as well as the thin thickness deposited. The micrograph was taken in no direct cross only for the so-called optically isotropy carbon clear. Now, the preferred orientation characterized by OA, determined by the described technique in this paper, is quantified adequately the anisotropy of the matrix without the restraint of layer thickness and optical activity compared with that by Ae. Each of the two low-textured carbons can be comparatively studied by their own OA. The analysis for the high preferred orientation in the 2nd layer has been mentioned in the above.

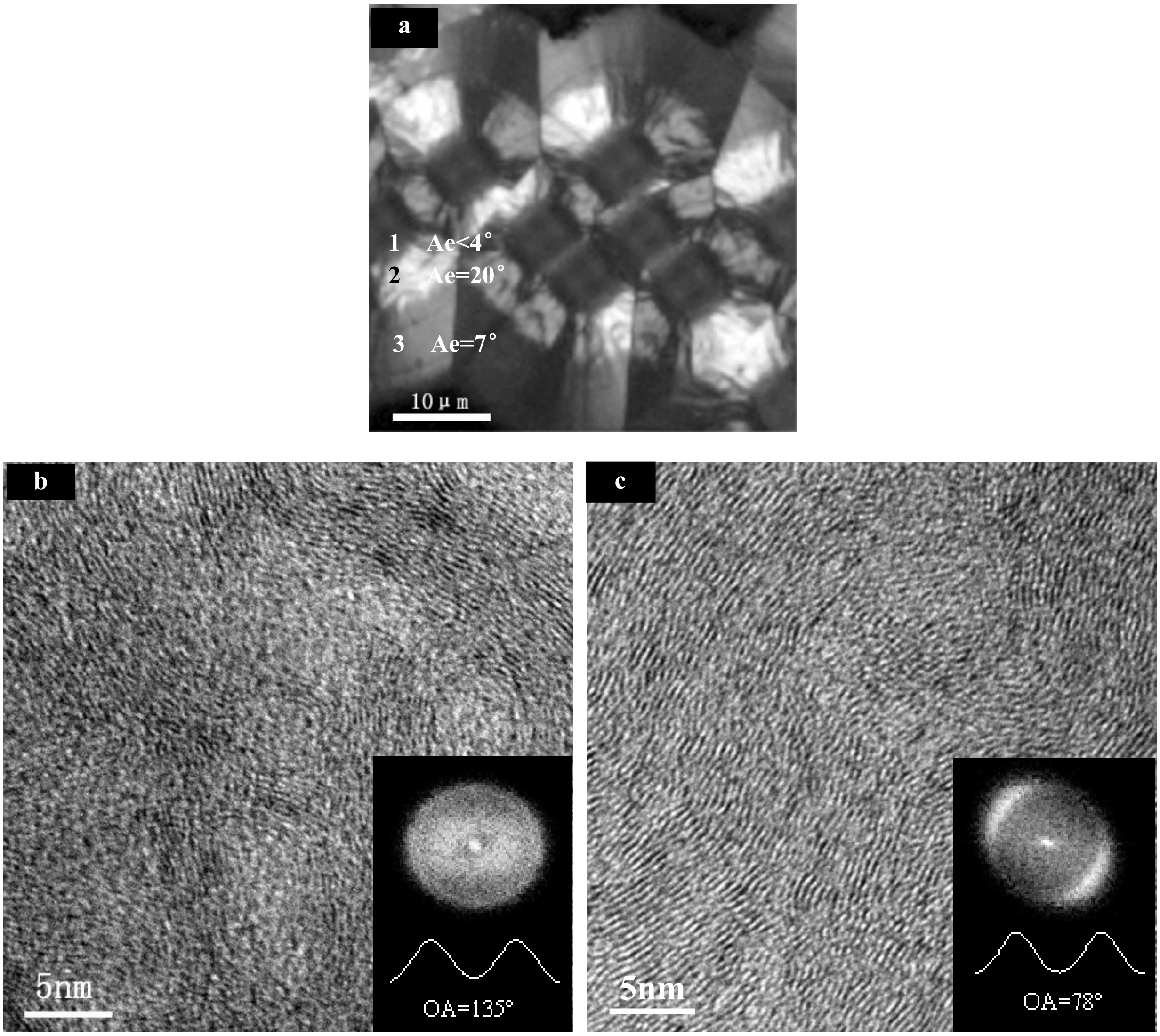
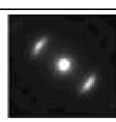
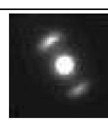
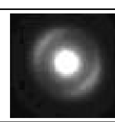
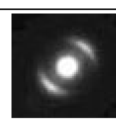
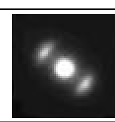
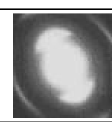
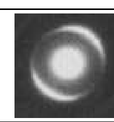
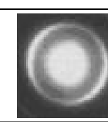


Figure 5. Comparative assessment of differently textured pyrolytic carbon layers by transmission electron and polarized light. The polarized light micrograph (a) with numbered 1 to 3 pyrocarbon layers was taken when an analyzer had a 4° departure from its direct cross location. The TEM 002-lattice fringes images, (b) and (c), corresponds to the 1st and the 3rd layer in (a). Insets in (b) and (c) are their own FFT each with Gaussian fit curve and OA value. The HRTEM with FFT of the 2nd layer is given in Fig.1.

Table 1 OAs of some SAED patterns published in Ref. calculated using the described measurement and reported by authors.

Diffraction patterns								
Reported *OA*	31°	39°	72°	55°	42°	50°*	86°	105°
Measured *OA*	28°	39°	73°	52°	40°	53-72°	84°	106°

The applicability and precision of the present work is further validated by the measurement to some SAED patters published by other researchers. The results from the applications are in general agreement with the OAs reported in the Refs. by comparing the data listed in Table 1. There is the 0~3° discrepancy in the OAs of each pattern from the two measurements excepting the pattern with * in Table 1. The cause of the small difference is considered that the patterns have changed with information losing in the course of image transformation or image transmission. On the other hand, the larger OA error for the pattern with * is probably brought by the variety of the radial location of the concentric ringed zone for sampling intensity owing its extremely elongated 002 arcs. The error presence is not caused by the measurement. Therefore, it can be declared that the designed system has great capability in the precise determination for OA.

Conclusions

An accurate method for the determination of the misorientation degree of pyrocarbons is described on the basis of the measurement of the orientation angle (OA) by HRTEM images or SAED patterns. The image pre-processing techniques, e.g., average filter, intensity adjusting, are proved proper to make the FFT image clear. The self-designed algorithms, including gray centroid method, polar axis scanning technique and Gaussian function, are effective in sampling intensity data and computing OA. Gaussian curves fit to the extracted intensity by iterative computations with least square errors. The initialization of Gaussian parameters depends on the meanings of OA. The system has been applied to the texture analysis of the multilayer matrices of the carbon/carbon composites fabricated by CVI. The results indicate that this approach allows differentiating pyrocarbons deposited under a wide range of size and optically anisotropy. The system precision is credible depending on a good agreement between the measured OAs and the reported data by testing the SAED patterns in literatures.

The measurement for obtaining OA from HRTEM images by performing the Fourier transform has the advantage to resolve the problem of a precise localization of the oriented areas. It also contributes to better assessment of the degree of anisotropy for the various pyrocarbons through the image analysis algorithms.

Acknowledgements

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