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Quantitative analysis of microstructure of carbon materials by HRTEM

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Abstract: The main object of the present research is to make a quantitative evaluation on the microstructure of carbon materials in terms of microcrystal. The digitized images acquired from finely pulverized carbon materials under HRTEM at a high magnification were processed by the image processing software so as to extract the fringes of (002) lattice of graphite crystal from the background image, and an FFT-IFFT filtering operation was performed followed by processes as binarization for the image and skeletonization for the fringes. A set of geometrical parameters including position, length and orientation was set up for every lattice fringe by calculating the binarized image. Then, the above obtained fringe parameters were put into an algorithm, which was especially developed for such fringe images so as to find fringes that could be regarded as those belonged to one single graphite microcrystal. The fringe was subjected sequentially to comparing procedures with every other fringe on aspects as parallelism, relative position and spacing, and the above comparisons were repeated till the last fringe. Eventually, the microcrystal size, its stacking number, and the distribution of the microcrystal in the whole sample, as well as other related structure information of such microcrystal in carbon materials were statistically calculated. Such microstructure information at nanometer level may contribute greatly to the interpretation of the properties of carbon materials and a better correlation with the same macrostructure.

Key words: carbon materials; microcrystal; digitized images; quantitative analysis; HRTEM

1 Introduction

Carbon materials have been confirmed to have turbostratic structure constituted by many graphite microcrystals. XRD technique is conventionally used to investigate the crystal structure and materials properties[1-3]. Some crystal parameters such as L_a, L_c and d-spacing can be calculated based on the results of XRD. Recently, with the occurrence of HRTEM (high-resolution transmission electron microscopy) technique, a visual view of such structure can be presented. SHAMA et al[4] reported layered graphite-like microcrystal of bituminous coal under HRTEM. RUSSELL et al[5] observed the coking transformation of Pittsburgh coal using HRTEM. In addition, quantitative image analysis has become one of the most successful laboratory techniques in materials science[6]. Based on stereology theory, data from a two-dimensional image can be converted into reliable and accurate structural information of three-dimension, which is a big stride from qualitativeness to quantitativeness. OSHIDA et al discussed the influence of conditions of HRTEM to the image processing and analysis with respect to carbon materials as fluorinated graphite fiber[7], activated carbon fiber[8] and amorphous carbon film[9]. HUANG Z H et al[10] displayed the nanopore structure of activated carbon fiber under HRTEM and obtained its fractal feature based on fractal theory. Other researchers[11-13] tried on the quantization of the crystal parameters of carbon materials, where some structural parameters were also obtained. Additionally, based on the results from image analysis, SHIM et al[14] focused on the orientation behavior of the graphite layer in carbon materials.

A main object of the present study is to develop a new statistical algorithm to determine the microcrystal units from HRTEM images of carbon materials. Based on the output of the algorithm, quantitative structural information, especially the distribution of microcrystals in carbon materials, is obtained. Another object of this research is to establish a new crystallinity index to characterize the degree of graphite crystals in carbon materials so as to make a correlation between the

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microstructure and the properties of carbon materials.

2 Experimental

Carbon materials samples, which were dispersed in ethanol, were obtained from Liulin coal (a bituminous coal) by coking process. JEM-2010(HITACHI, Japan) was work at an accelerating voltage of 200 kV. Carbon materials powders that were suspended in ethanol were chosen as carbon materials samples and were carried by a copper grid and transferred into the observation chamber of JEM-2010 microscope. After the system was evacuated to a vacuity of 1.33×10^{-4}–1.33×10^{-2} Pa, the samples were first examined at a moderate magnification such as 100 K× or 200 K× to find wedge-shaped fragments that had edges thin enough (tens of nanometers typically) for the electron to pass through so as to meet the imaging condition. Under the high magnification of 500 K×, 10 or more such edge regions for one sample were then selected and photographed when a clear fringe image was imaged.

Images from the microscope were stored directly into a PC as a digital format (RAW) with 1 024×1 024 pixels and a 8-bit grayscale. The size of the digital image corresponds to a real size of 39 nm×39 nm, which means that one pixel on the image represents a real size of about 1/26 nm. Fig.1 shows some example images thus-obtained. Due to the limitation of the current sample preparation technique, however, the superpositions of fringes are sometimes unavoidable, as shown in Fig.1(c) typically.

3 Image processing

The first challenging task for the quantitative analysis of TEM fringe images is the conversion of the complex original image into a set of distinct, identifiable fringes that can be analyzed by object-oriented image analysis algorithms. Here, based on the prior image processing methodology, an improved processing procedure that can separate fringes with excellent reproducibility is developed. Thereby, the difference between fringes can be revealed, and identification on these fringes can be carried out effectively and objectively. Fig.2 shows the specific processing steps especially designed for fringes image of the present research, wherein step of filtration, step of conversion and step of skeletonization are described in detail as follows. The processing software used here is ImageJ v1.30 from National Institutes of Health, USA.

3.1 FFT Filtration

One of the key means for extraction of fringes used here is FFT filtration, which is capable of removing the noise of no interest without losing the information of fringes. Fig.2 gives the flow diagram of image processing on lattice image of carbon materials. Fig.2(b) gives a frequency domain showing a frequency distribution of the original image (Fig.2(a)) after being subjected to a Fast Fourier Transform (FFT), wherein farther it is from the center, higher the frequency is. In Fig.2(b), there are two concentric arcs with a relatively higher brightness, which are actually two segments of one similiar circular ring. It is a typical diffraction pattern of the multicrystal, which is the result of the diffractions superposition of countless micro single crystal grains. In a case where the arrangement of these single crystals is totally random, there will be an intact ring shape for thediffraction pattern. In the present case, however, only two symmetrical segments of the ring are presented. That is to say, the arrangement of single crystals exhibits an orientation preference, which is inversely proved by the original crystal lattice image(Fig.2 (a)).

Based on the above facts, by using the reversibility of Fourier Transform, a filtering process can be easily operated. To achieve such object, with respect to the frequency domain, the portion (frequency) other than the region where the circular ring represented the ordered structure to be located was deleted, i.e. covered by pure

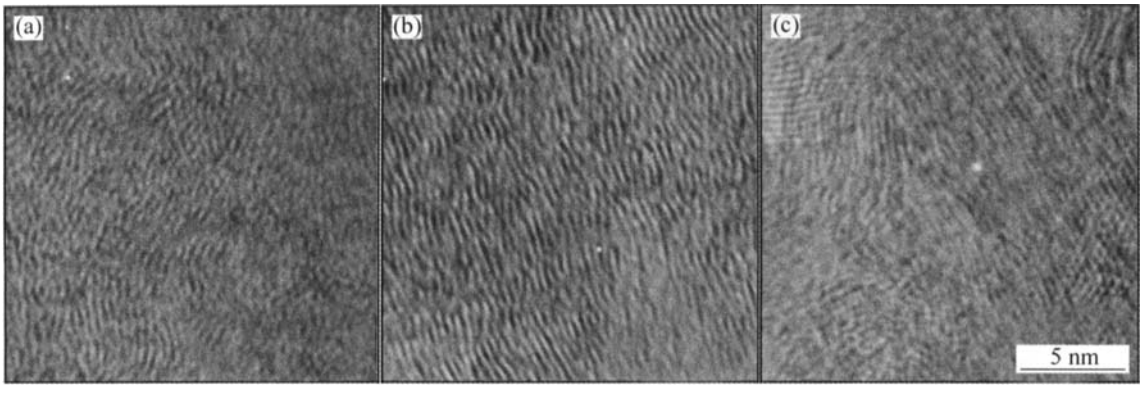

Fig.1 Some typical fringe images of carbon materials by HRTEM