

# APPLICATION OF X-RAY MEASUREMENTS FOR CHARACTERIZATION OF ARTIFICIAL CARBONS

E. FITZER, K.-H. KÖCHLING, G. SCHWARZ

Institut für Chemische Technik  
Universität Karlsruhe, W.Germany

## Introduction

The paper is concerned with characterization of commercially important carbon materials by X-ray diffraction analysis. As well-known there exist careful investigations on the effects of microstructure of homogeneous carbons on their diffraction behaviour, although the objective valuation of the different structural models used for interpretation of experimental average diffraction data is still difficult. Additional problems arise from the heterogeneity of carbon and graphite samples as far as the degree of order of the different parts within the specimen is concerned. This problem of questionable significance of experimental data for characterization of heterogeneous samples is hardly studied systematically until now, and no international agreement exists about guidelines for practical application. The present work should contribute to the efforts of IUPAC commission on "Characterization of Carbon".

Under the same experimental conditions integral intensity of diffraction lines of ordered and disordered carbon can vary within orders of magnitude. As in carbon technology mostly heterogeneous mixtures of various carbons must be characterized, for example filler and binder carbons within one sample, the superficial interpretation of sharp diffraction lines as representative average can be misleading and can simulate a higher degree of graphitization even in case of minor contents of well graphitized particles.

## Literature

Already 1960 it was tried to analyse mixtures of non graphitizing carbon with natural graphite by the intensity ratio of (001) lines, at various angles (H. BEUTELL et al, 1973). Although this method is suitable in particular cases (W. WEISWEILER et al. 1971), principal limitations arise from the use of a non graphitizing matrix in such reference material. Therefore the present experiments are based on graphitizable coke with varied heat treatments as main constituent of the sample.

## Experimental

Sample material was prepared by mixing pre-heattreated powder of coal tar pitch coke with additions of 0 (0.1) 2 (1) 10 (5) 50 wt.-% of natural graphite flakes (Ceylon),  $c/2 = 3.354 \text{ \AA}$ , polycrystalline graphite,  $c/2 = 3.359 \text{ \AA}$ , and microcrystalline graphite (Kaisersberg),  $c/2 = 3.357 \text{ \AA}$ , as listed in tab.1. Ni-filtered Cu-K $\alpha$ -radiation with BRAGG-BRENTANO-arrangement and planar samples were used for the diffraction measurements. Sample thickness was optimized by experiments (50 mg/cm<sup>2</sup>, corresponding to a

sample thickness of 0,25 mm), because numerical correction of the absorption effect is too difficult in case of heterogeneous targets.

## The effect of sample heterogeneity on (001)-diffraction lines

In order to describe the effect of the two different carbon types within the various samples we will distinguish between three limiting cases as shown in fig. 1.

- Case A: The appearance of two clearly separated diffraction lines.
- Case B: Superposition of both lines with the possibility of easy separation for evaluation of the single diffraction profiles
- Case C: Superposition of both lines without the possibility of visual separation

The experimental results are compiled in fig. 2. The added amount of well graphitic component is indicated as abscissa. No difference in diffraction lines between mixtures with natural graphite flakes and well-graphitized artificial carbon was found as far as samples with additions up to 10 wt.-% are considered.

In the case of glass-like carbon small additions of graphitized samples (about 0,1%) can be detected already. In the case of tar and pitch coke as main constituents of samples the lower limit for semi-quantitative estimation of well graphitized parts is found to be in the order of 0,2%.

The upper limit of the addition causing separate lines according case A is found to be 10% approx. for the (002)-interference. The limits for the second order of the (001)-interference are indicated by dotted lines being between 0,3 and 12-15%.

The ordinate of fig.2 indicates maximum heat treatment temperatures of the pitch coke component of the samples. In all cases a heat treatment time of one hour was used. Already heat treatment at 1700°C causes superposition of the diffraction lines according to case B at every percentage of the addition. Easy separation is still possible in samples with graphitic additions between 0.2 and 10%. With increasing heat treatment temperature the composition suitable for easy analysis by (001)-lines is shifted to higher contents of additive, i.e. for 1900°C heat treatment temperature between 1 and 20 wt.-%. The same effect is valid for the analysis of the (004)-lines.

If heat treatment temperatures above 2200°C were applied, complete superposition of both lines was found in all cases according to case C, however, with the possibility to estimate the content of well graphitized

additions by the asymmetry of the base-line if additions between 3 and 20% are considered. If higher contents of well graphitized parts are present there exists no possibility for estimation by analysis of the base-line.

#### Effect of sample heterogeneity on (hkl)-diffraction lines:

As known modulation of two-dimensional reflections of non graphitized carbons is caused by heat treatment above 2000°C. This is valid for (10)- and (11)-reflexions. (10) two-dimensional reflexions are strong enough to be found in nearly all types of samples, whereas (11)-lines can hardly be seen in non graphitized carbons. Therefore (110)- and (112)-lines were selected for indication of graphitized parts because no superposition by (11)-lines is to be expected. Three-dimensional (110)- and (112)-lines can be seen in case of non heat treated matrix material if additions of at least 10 wt.-% are used. Below this limit no quantitative evaluation is possible. According to our experimental results quantitative estimation of at least 50% well-graphitized carbon is possible by calibrating the intensity of three-dimensional interference against the intensity of the base-lines with an accuracy in the order of  $\pm 5\%$ . As can be seen from fig. 2 the evaluation of these (110)- and (112)-lines can be regarded as a supplement to the results from analysis of the base-lines.

With increasing heat treatment temperature the quantitative evaluation of the three-dimensional diffraction lines becomes more difficult and is completely impossible if heat treatment temperatures above 1900°C were applied because of the graphitization effect of the pitch coke and the resulting modulation of (11)-lines of the main part of the samples (see range II in fig.2).

The area III in fig.2 covers compositions of samples in which the content of added well graphitized part is too low to enable a distinction between the addition and the effect of matrix graphitization.

#### Conclusions

The applicability of the methods described above for characterization of heterogeneous carbon and graphite samples will be discussed in detail. Industrial samples with varied types of filler and binder carbons, or filler carbons of original high sulfur content after heat treatment above puffing temperatures, non graphitized carbon with stress graphitized binder contents and finally the effect of catalytic graphitization in various sample materials will be described in more detail.

#### References:

M. BEUTELL, E. FITZER, R. GAIN, O. VOHLER (1963); Proceedings of the 5th Carbon Conference, Vol. II, pp. 319 - 333

W. WEISWEILER, W. BRAUN (1971); Carbon Vol.9, pp. 457 - 465

HTT of the coal tar pitch coke	used diffraction lines
1300°C, $\bar{c}/2 = 3,450 \text{ \AA}$	002, 004
1650°C, $\bar{c}/2 = 3,435 \text{ \AA}$	
1900°C, $\bar{c}/2 = 3,405 \text{ \AA}$	
2200°C, $\bar{c}/2 = 3,390 \text{ \AA}$	002, 004, 110, 112

Tab. 1: Compilation of coke-HTT and X-ray interferences

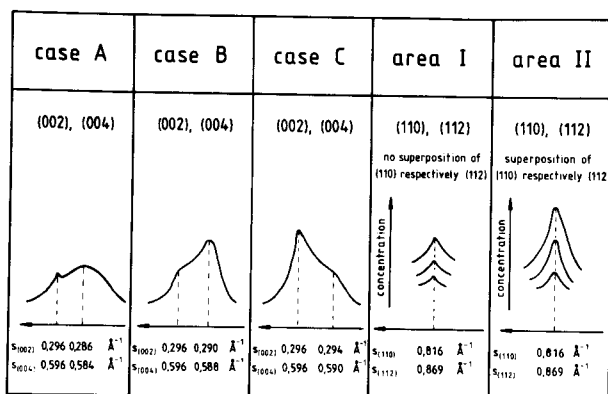


Fig.1: Position and shape of X-ray interferences as function of the graphite content and HTT of the samples (see fig.2)

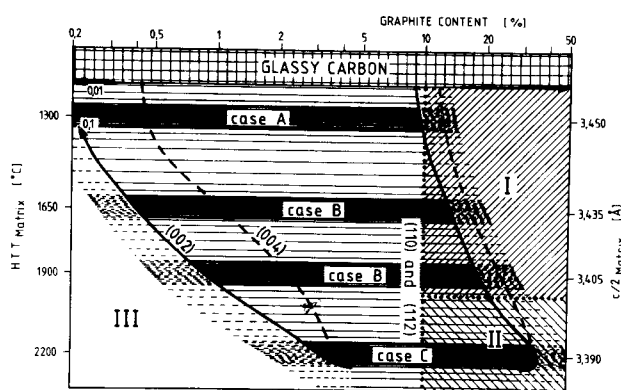


Fig.2: Applicability of the different X-ray interferences (see fig.1) on characterization of heterogeneous carbons