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COMPARATIVE MICROSTRUCTURAL ANALYSIS OF NON-GRAPHITIC CARBONS (NGCS) BASED ON WIDE-ANGLE X-RAY (WAXS) / NEUTRON (WANS) SCATTERING & PAIR DISTRIBUTION FUNCTION (PDF) ANALYSIS

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Introduction

Non-graphitic carbons (NGCs), a million-ton-scale class of sp^2-hybridized carbon materials, are of significant relevance for several applications, e.g. adsorption/separations, current transmission, and carbon materials production. They comprise a plurality of carbons such as activated carbon, glassy carbon, etc. NGCs are made up of small graphene layer stacks, with the layers arranged turbostratically and the stacks displaced and distorted to each other. This lack of long-range crystallographic order causes broad and overlapping reflections in WAXS and WANS. The general NGC structure is shown in Figure 1 and described among others by the structural parameters L_c and L_a which are the stack height and the average lateral extension, respectively. Further important and relevant parameters are the C-C bond length, the average distance a_3 between the layers and parameters quantifying the substantial degree of disorder in the stacking and the layers themselves. A quantitative description of this disordered sp^2 polyaromatic microstructure is essential to link it to macroscopic material properties and to optimize production processes.

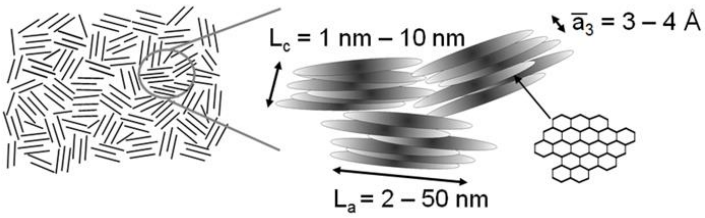

Figure 1: Basic NGC structure - stacks made up of a turbostratic arrangement of graphene layers. Adapted from[1].

In 2002 Ruland and Smarsly introduced a novel approach for WAXS data evaluation of NGCs[2], which provides quantitative structural characterization of NGCs. However, the analysis of NGCs by WAXS and thus its validity generally suffers from experimental and physical limitations, e. g. damping of WAXS by the atomic form factor at large scattering vectors and incoherent scattering. As WANS is not impaired these effects, analyzing WANS data of NGCs provides fundamental advantages. Here we address the issues of how the most relevant structural parameters are affected by typical shortcomings of powder WAXS lab analysis, if the parameters describing size und disorder can be accurately separated, if a meaningful, precise characterization of the structure of NGCs possible by standard WAXS setups, how disordered NGCs are in relation to graphite and what the nature of this disorder is.

Materials and Methods

For this study several different NGC samples were synthesized by carbonizing different precursors (CB - carbon black, AC - acetylene coke, PF-N - Novolac resin, PF-R - resole resin, MP - mesophase pitch, LSPP - low softening point pitch) at different temperatures (denoted in each sample abbreviation in units of °C). WAXS/WANS curves of these samples were acquired using a standard laboratory X-Ray diffractometer / at the neutron scattering facility of Helmholtz-Zentrum Berlin. WAXS pattern for PDF analyses were acquired at the Diamond Synchrotron (UK). After data acquisition, first data analysis of the WAXS/WANS curves was performed by fitting a theoretical scattering curve to the respective data using Ruland's and Smarsly's model for WAXS/adopted for WANS. The analysis yielded the microstructural parameters mentioned above, which were compared in terms of differences between parameters derived from WAXS/WANS. Second, by fitting simulated WAXS/WANS curves being impaired both by different noise levels and 2θ-cut-offs, we investigated how reliably the originary microstructure can be reconstructed from WAXS/WANS. Third, we performed a PDF analyses based on the WAXS pattern collected at Diamond and fitted the PDF curves in order to extract a particle dimension thereof to compare these with the respective L_a values.

Results and Discussion

In Figure 2 the obtained microstructural parameter L_c from both WANS and WAXS data analysis is presented. This parameter as well as L_a, a_3 and the C-C bond length, all describing structural dimensions mostly overlap within their respective error margins. Both Lc increases if the same precursor is carbonised at a higher temperature. The non-graphitizing resin precursors yield NGCs with lower L_c values even if carbonised at same or higher temperatures than graphitizing pitch precursors. Carbonising low softening point pitches produces NGCs with larger L_c values than carbonising mesophase pitches at higher temperatures. The disorder parameters, however, deviate. As the WANS data display a larger number of reflections due to their larger s-range allowing for a clearer separation of size and disorder effects and possess an enhanced data quality in terms of physical limitations, the values derived from WANS data should be considered more trustworthy.

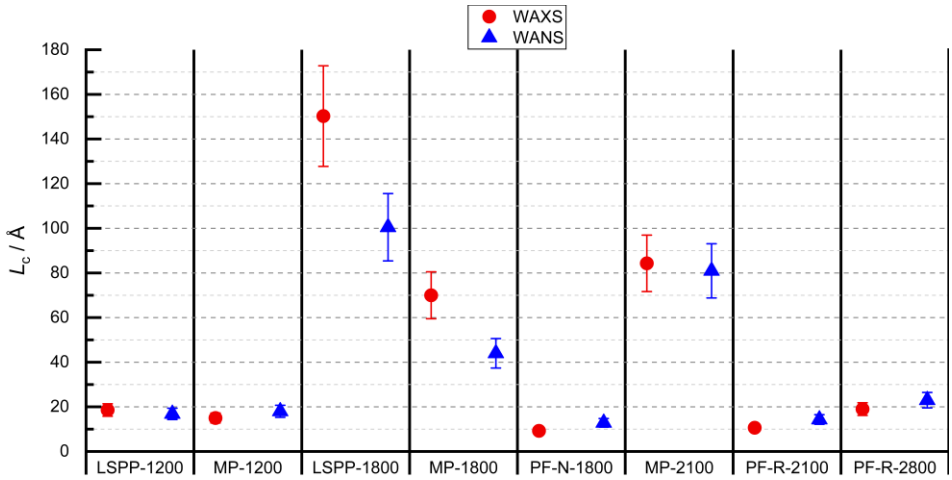

Figure 2: Comparison of the microstructural parameter L_c for eight samples, graphitizing (LSPP-1200, MP-1200, LSPP-1800, MP-1800 and MP-2100) and non-graphitizing ones (PF-N-1800 and PF-R-2100, PF-R-2800), obtained from WANS and WAXS analysis using the approach of Ruland and Smarsly. This size parameter mostly matches within the respective error margins.

As a main result of fitting impaired simulated WAXS/WANS data, we found that data noise generally exerts a larger negative impact on the WAXS/WANS analysis than a limited s-range, while the precision in the parameter values is higher for WANS compared to WAXS. Unfortunately, especially the most relevant parameters are associated with a significant error in the range of ca. 10 % in case of medium data noise. However, such precision is sufficient for semiquantitative comparisons among similarly treated materials, e.g. as a function of temperature. Hence, as a main finding even standard laboratory WAXS instruments, using the averaged Cu-K-α wavelength of 1.5418 Å, will provide a sufficient data quality for determining these parameters with the precision needed for a meaningful interpretation.

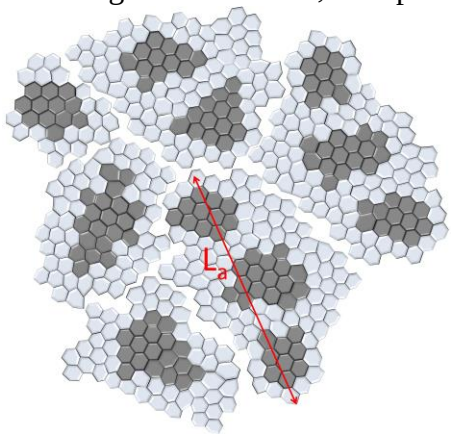

Figure 3: Assumed structures of the graphene layers found in NGCs. Either only one highly ordered core is surrounded by a less ordered shell or more than one ordered core is present. (The figure is not true to scale.)

The main result from the PDF analyses is on the one hand that all samples investigated exhibit a high degree of order within the first few benzene rings, with the maxima of PDF function matching those of graphite quite well, and significant dampening indicating substantial disorder at larger distances On the other hand, we found the particle dimensions extracted from the PDF to be substantially smaller than the layer size indicated by L_a being convertible in a diameter D which is similar to L_a itself ($L_a = 0.85D$). On these qualitative findings we conclude that the WAXS/WANS fitting and the PDF analysis speak for a peculiar structure of the graphenes, and we propose a structural model for NGCs as depicted in X, which goes beyond the previously favored view on the structure of NGCs. In this model, each layer is divided in one or more highly ordered domains ("core(s)") surrounded by a less ordered region within one graphene. These "core" domains typically extent several benzene rings as revealed by the PDF analysis.

Conclusions

Several NGC samples were analyzed by evaluation of their WAXS/WANS patterns using Ruland's and Smarsly's modell as well as PDF analyses. In addition, impaired simulated WAXS/WANS curves were. The two main findings are first that standard laboratory X-ray diffractometers provide data of sufficient quality for NGC microstructural analysis and second that NGCs seem to exhibit a peculiar structure going beyond the previously favored view on the structure of NGCs.

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