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Simulation of X-ray powder diffraction patterns for low-ordered materials

S.V. Cherepanova*, S.V. Tsybulya

Boreskov Institute of Catalysis, Prosp. Ak. Lavrentieva 5, Novosibirsk 630090, Russia

Abstract

A new program for simulation of X-ray diffraction patterns of polycrystalline materials with different kinds of imperfections has been developed. These calculations are performed on the base of the model of one-dimensional (1D) disordered crystal being the statistical sequence of the biperiodic layers. Each layer is characterized by its structure, thickness and probability of occurrence. The sequence of layers is specified with the use of order–disorder parameters and some probability coefficients. Such defects as small sizes of coherently scattering domains (CSD), microstrains and stacking faults are taken into account. Our program simulates two kinds of layers: isotropic (circle) and anisotropic (rectangle). Along with mean sizes of CSD, the variances of normal or lognormal size distributions of CSD can be taken into account. Also, the program makes it possible to specify whether the fluctuations in the layer position are correlated or not. The plane groups of symmetry are introduced to reduce the run time. The background is approximated by using the smoothing spline-functions. The correction for instrumental line broadening is calculated with a standard. Simulated diffraction pattern is compared and fitted for best correspondence with the experimental one.

Real structures of some specimens have been investigated with this program. These are metastable Ni–In alloys prepared by mechanochemical synthesis, filamentary carbons and metallic Co with microdomain structure.

Keywords: Powder X-ray diffraction; Full-profile analysis; Real structure; Stacking faults; Microstrains

1. Introduction

Nanocrystalline materials attract close attention of researchers because of their physical and chemical properties and widespread use in the different fields of science and technology. Among them, a particular type of objects is represented by the systems with developed surface and strongly disordered bulk structure; those that are intermediate between crystal and amorphous materials. As examples of such systems, there are «amorphous» carbon materials with CSD sizes less than 5 nm, metastable solid solutions of metals prepared by mechanochemical alloying, weakly ordered oxides synthesized in the significantly non-equilibrium conditions at low-temperature decomposition of salts and hydroxides as well as by mechanochemistry and plasmochemistry. The structure of such partially dissociated states can be characterized only by the combination of three-dimensional (average) periodic structure parameters and real structure

* Corresponding author. Tel.: +7-83832-341300; fax: +7-83832-343056.

E-mail address: tsybulya@catalysis.nsk.ru (S.V. Cherepanova).

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parameters (the degree of microstrains, the density of dislocations, the concentration of stacking faults, the CSD sizes in relation to real sizes of nanocrystalline particles).

X-ray diffraction (XRD) remains the basic method for solid structure investigation. In the last years, the capabilities of this method are extended due to development of computer machinery and new software algorithms. The XRD method can give information about phase composition of catalysts, their crystal structure, presence/absence of the defects, etc. But traditional techniques of X-ray structural analysis of polycrystalline materials are limited by some parameters of the materials such as small concentration of defects and CSD sizes exceeding 5 nm.

The aim of this work is to develop the method of full-profile analysis of XRD patterns of dispersed and partially disordered systems, to work out the appropriate software for the investigation of a number of systems, which are actual for catalysis.

2. Theory

We used the currently developed approach to calculate directly the XRD patterns based on the model of 1D disordered microcrystals of real sizes [1]. The structure of 1D disordered crystal can be represented as a statistic sequence of biperiodic layers with a random or regular distribution of the interlayer translations. Parameters of the model are as follows: the number of the layers and their sizes or parameters of CSD distribution over the number of layers and their sizes, the probability of stacking faults (for the structures of close packing) or the probability of defects of layer sequence and/or their displacement (for lamellar structures), parameters of distribution of random interlayer translations that characterize microstrains of different types. In spite of the evident advantages of such method for the investigation of disordered structures, it has not received wide acceptance up to now due to the complexity of the mathematical description and program algorithms.

3. Results and discussion

We developed a computer program for investigation of the real structure for the wide range of objects including such special cases such as: (a) crystals with the developed micrograin structure and crystals of very small physical sizes (model of the crystal of limited sizes and definite shape with some refined parameters such as probability of stacking faults, degree of microstrains and parameters of size distribution); (b) paracrystals (model of infinitely large crystal with «accumulated» fluctuations in layer positions — microstrains of second type); (c) turbostratic structures (model of layered crystal with the random shifts and rotations of layers); (d) polytypic and modulated structures of different kinds as well as a number of real systems for which different reasons for the disruption of long range order take place simultaneously. The method proposed is useful for the simulation of diffraction patterns of materials having very small sizes (2–3 layers of 1.5–2 nm in diameter) and the accuracy range being between 5 and 20 nm.

With the use of this new method of full profile analysis of XRD patterns, the investigation of the structure of the dispersed and disordered carbon graphite-like materials has been performed. The systematic analysis of the influence of disruptions of sequence of graphite layers and their regular superposition has been carried out. The diffraction patterns transformations expressed in broadening and/or shift of definite peaks, intensity redistribution and/or appearance of new diffraction lines have been established in accordance with the type of disruption, that makes possible to identify different types of structural disorder [2]. For several samples of filamentary carbon materials, the structural refinement has been carried out. An example of refinement is illustrated in Fig. 1. Curves

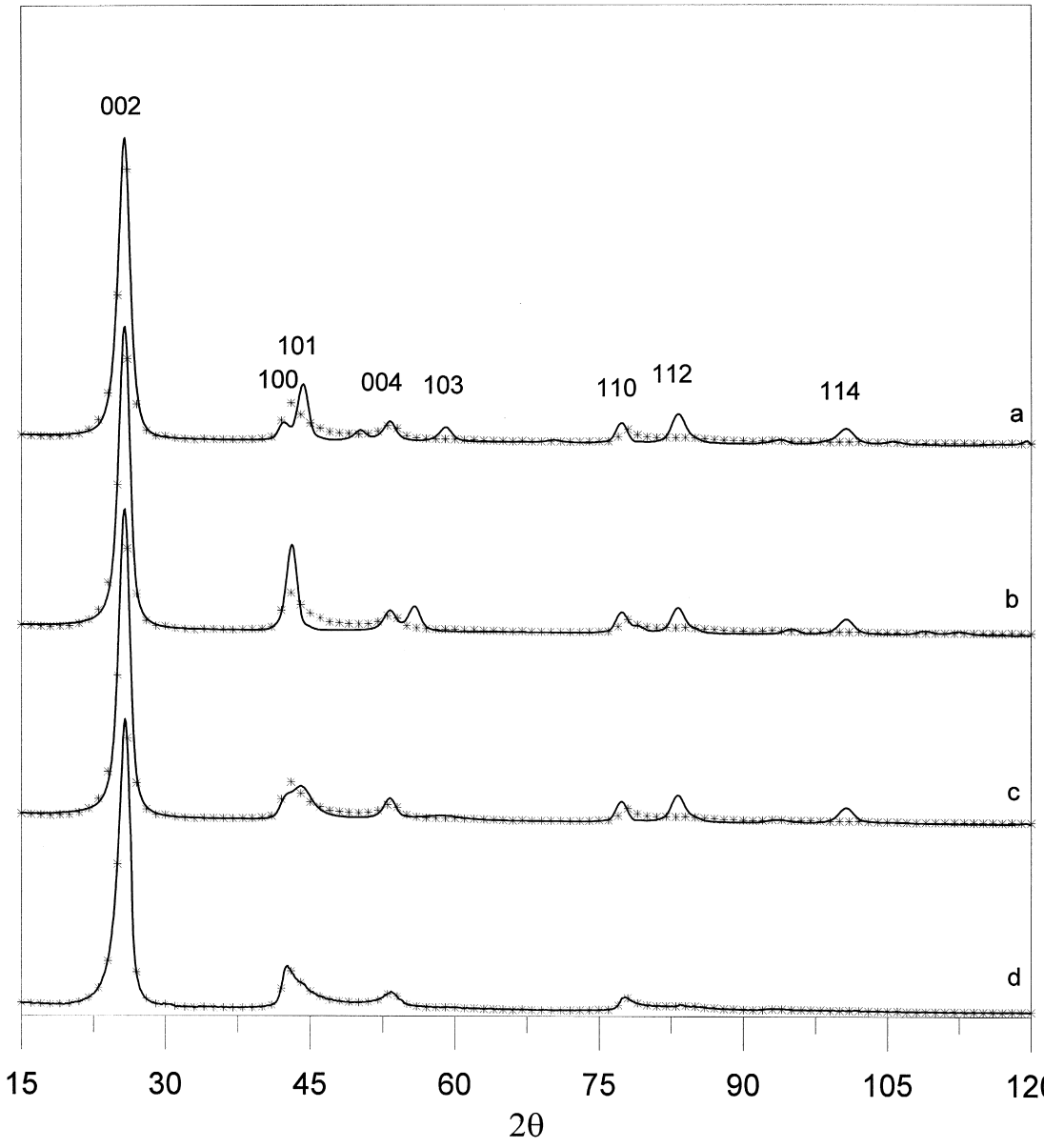

Fig. 1. XRD patterns of filamentary graphite-like carbon: observed (∗) and calculated (—) for different models 2H-polytype (ABAB...); 3R-polytype (ABCABC...); random sequence of A, B, C layers; random sequence of A, B,C layers with fluctuations in their positions.

a and b in Fig. 1 demonstrate the theoretical XRD patterns for the ordered graphite 2H-(ABAB...) and 3R-polytype (ABCABC...), respectively. As evident from this figure, they are significantly different from the experimental pattern. C curve shows the XRD pattern calculated for the random sequence of A, B, C graphite layers. In this case there is also a clear difference between the observed and calculated patterns especially in the angle range of 2θ over 70°. Good correspondence between the experimental and theoretical diffraction patterns is observed for the model including the statistic deviations of graphite layers from their regular

positions. Such type of disorder results in the disappearance of the diffraction lines with 11L Miller indexes and their transformation into diffusion scattering in the simulated XRD pattern that is similar to experimental one (Fig. 1d).

The simulation of diffraction patterns of metals with cubic and hexagonal close packing structures with different types of defects has been carried out. It has been demonstrated with an example of Ni–In supersaturated solid solutions that this method can be applied for the simulation of the materials of paracrystalline-like structure, i.e., the objects in which significant microstrains lead to the lack of the long range ordering without breakdown on the separate micrograins [3].

When investigating cobalt metallic catalysts in the reaction of CO disproportionation, Khasin et al. [4] have found that the structural transformation of Co particles of size more than 25 nm takes place. We have shown [5] that the structure of Co particles after catalytic reaction and carbon deposition can be described as a statistic sequence of the coherently connected microdomains of two types having structures of cubic and hexagonal closed packings. The method permitted us to set up a quantitative relationship between these microdomains and evaluate their average thickness.

4. Conclusions

Thus, the proposed method of the full profile analysis of XRD patterns can be usefully employed for the study of the real structure of nanocrystalline materials, those being of interest for the solid chemistry and catalysis. With the use of this method, a qualitative data on the nature of crystal structure imperfections can be obtained, and concentration of the structural defects of different types and sizes of CSD and degree of microstrains can be determined.

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