



High-resolution neutron diffraction study of microstructural changes in nanocrystalline ball-milled niobium carbide NbC_{0.93}



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ABSTRACT

High resolution neutron diffraction was applied for elucidating of the microstructural evolution of nanocrystalline niobium carbide NbC_{0.93} powders subjected to high-energy ball milling. The diffraction patterns were collected with the high resolution Fourier diffractometer HRFD by using the reverse time-of-flight (RTOF) mode of data acquisition. The traditional single diffraction line analysis, the Rietveld method and more advanced Whole Powder Pattern Modeling technique were applied for the data analysis. The comparison of these techniques was performed. It is established that short-time milling produces a non-uniform powder, in which two distinct fractions with differing microstructure can be identified. Part of the material is in fact milled efficiently, with a reduction in grain size, an increase in the quantity of defects, and a corresponding tendency to decarburize reaching a composition NbC_{0.80} after 15 h of milling. The rest of the powder is less efficiently processed and preserves its composition and lower defect content. Larger milling times should have homogenized the system by increasing the efficiently milled fraction, but the material is unable to reach a uniform and homogeneous state. It is definitely shown that RTOF neutron diffraction patterns can provide the very accurate data for microstructure analysis of nanocrystalline powders.

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1. Introduction

The quantification of microstructural features such as shape and size of the crystallites, their distribution, and the type/quantity of defects is a necessary step to understand the behavior of a nanosized powder in order to manufacture and utilize it. The analysis of fine-grained materials therefore requires an accurate assessment not just of the structure but also of the microstructure, using fast, reliable and unbiased techniques. Among the available techniques to obtain this information in a non-destructive way, diffraction certainly plays a leading role, especially considering the big progress that the technique made in the last decades [1,2].

The methods nowadays available for the retrieval of microstructural information from diffraction data may be divided in two classes: one includes those techniques based on the study of some integral characteristics of the diffraction peak profiles (e.g., the breadth), while the other considers the methods aimed at modeling the diffraction pattern as a whole.

The Scherrer equation [3] and the Williamson–Hall plot [4] are probably the most common exponents of the first class, as the microstructure

(in terms of an “average crystallite size” and a “microstrain”) is directly obtained from the integral breadths of individual diffraction peaks. The Rietveld method [5] and the Whole Powder Pattern Modeling (WPPM) [6], conversely, take the whole pattern into account trying to interpret it in terms of physical models, respectively, for structure and microstructure. So far, the WPPM is the only method based on accurate models for the microstructure and can directly include the parameters of the size distribution of crystallites into the refinement procedure [7].

Most of these techniques are routinely employed for the analysis of X-ray data; neutron diffraction is seldom considered. This is astonishing, as neutron TOF (time-of-flight) diffractometers operational at pulsed sources have a great potential for the characterization of the microstructure of fine-grained materials. Their resolution function, in fact, is almost independent of scattering vector Q within a fairly wide range. This is certainly quite different from the conventional neutron diffractometers using a monochromatic beam where the resolution function $R(Q)$ is close to parabolic with a rapid rise in the both directions from the minimum value. In addition, the application of correlation Fourier technique on pulsed neutron source and the realization of the so-called reverse time-of-flight (RTOF) data acquisition method make it possible to achieve very high resolution comparable with that of X-ray instruments while maintaining the short source-to-detector distance and, consequently, the high brightness. The resolution of RTOF

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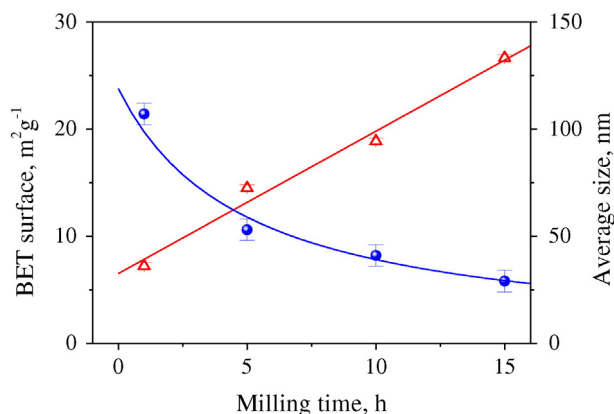


Fig. 1. Dependence of the specific surface area of the NbC_y powders (triangles, left scale) and the average crystallite size (circles, right scale) on the milling time, as defined by BET method.

diffractometer mostly depends on the maximum rotation speed of the Fourier chopper, and can be tuned for specific purposes. Diffraction peaks obtained on such an instrument should be symmetric, without long 'tails' observed on diffraction spectra from conventional TOF instruments, installed at spallation neutron sources. This fact greatly simplifies precise peak profile analysis.

In a previous short Letter [8] it was shown how microstructural information can be extracted from TOF data using the modified Williamson–Hall method. In particular, for cubic niobium carbide NbC_{0.93} it was found that a correct interpretation of the diffraction data is not possible without the account for the anisotropic peak broadening due to microstrain. But the result of the investigation [8] was ambiguous, as the observed diffraction line profiles could not be accurately reproduced within the framework of the applied simplistic model.

We have carried out additional experiments on the same material and further analysis using more advanced line-profile analysis methods.

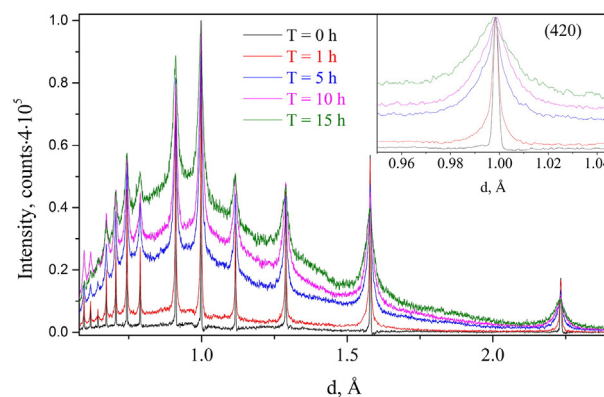


Fig. 3. Neutron diffraction patterns of the NbC-n powders, n = 0, 1, 5, 10, 15, measured with HRFD. As the milling time increases, the peak widths and the incoherent background increase as well. Inset shows the evolution of peak (420) profile with increasing milling time. Initial patterns are normalized by the maximum intensity value for (420) reflection.

This helped reaching an excellent agreement between experiment and model, which reveals important aspects of the microstructure of powdered nonstoichiometric niobium carbide, and allows understanding of its evolution during the milling process. Consequently, the focus of this paper is to demonstrate the application of advanced line profile analysis methods to the neutron diffraction data and to validate the possibility to use the high-resolution TOF neutron diffraction for the precise characterization of the microstructure of nanomaterials.

2. Samples and experiment

Niobium carbide powder with nominal composition NbC_y, y = 0.93, was subjected to high-energy ball milling. Each time 10 g of initial NbC_y powder was milled at 500 rpm in a Retsch PM-200 mill using the total of

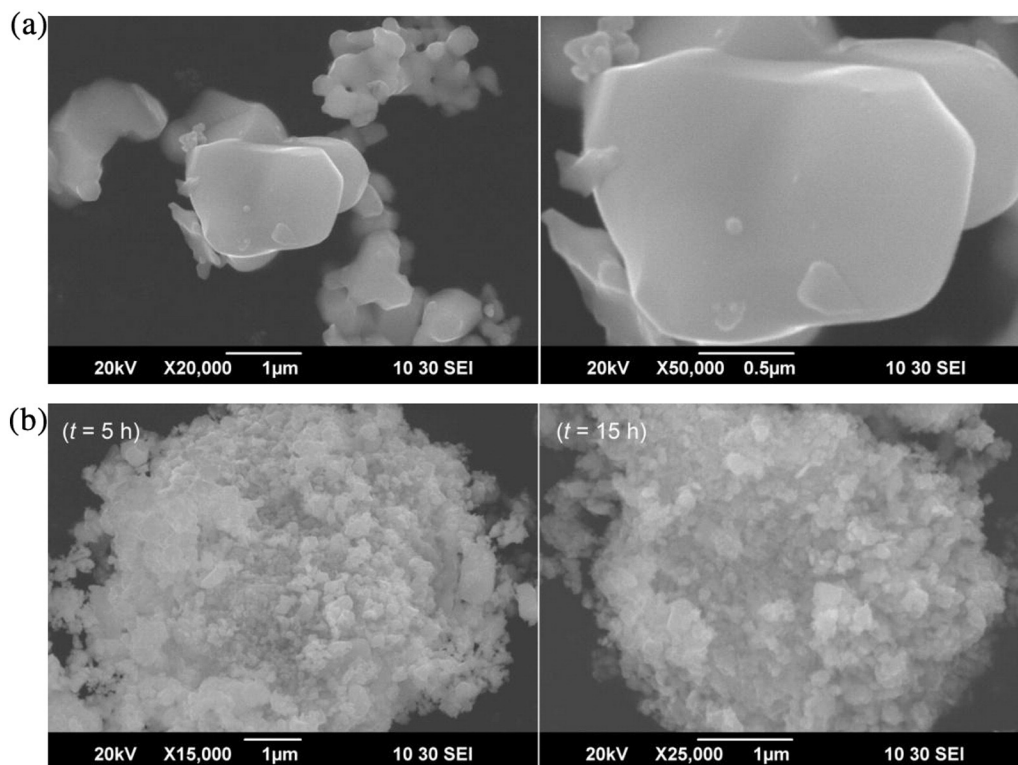


Fig. 2. a) SEM images of the initial coarse-grained powder of NbC_{0.93} niobium carbide at different magnifications. b) SEM images of NbC_{0.93} nanocrystalline powders produced by ball milling during 5 h and 15 h. Figures a (left) and b are reprinted from [11] with permission from Elsevier.

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