Neutron Diffraction Study of Microstructure of Nanocrystalline Cubic Niobium Carbides from NbC$_{0.77}$ to NbC$_{0.96}$

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Authors’ contributions

This work was carried out in collaboration among all authors. Authors ASK, AMB and AIG designed the research. Authors ASK and AIG prepared the samples. Authors VSK and IAB performed experiments on the high-resolution neutron diffraction. Authors AMB and AIG managed the analysis of the study. All authors wrote, read and approved the final manuscript.

ABSTRACT

The microstructure of nanocrystalline nonstoichiometric niobium carbides NbC$_{0.77}$, NbC$_{0.84}$, NbC$_{0.96}$ powders produced by high-energy ball milling has been investigated by time-of-flight (TOF) high resolution neutron diffraction. The diffraction patterns have been collected with the high resolution Fourier diffractometer HRFD by using the TOF mode of data acquisition. The nanocrystalline ball-milled powders have a microinhomogeneous structure, in which two fractions with different particle size and composition can be identified. The average sizes of the coherent scattering regions and microstrains in nanocrystallites with allowance for the anisotropy of the deformation distortions have been estimated. It is shown that TOF neutron diffraction patterns can provide the very accurate data for microstructure analysis of nanocrystalline powders.

Keywords: Time-of-flight neutron diffraction; high-energy ball milling; niobium carbide; nanocrystalline materials; microstructure.
1. INTRODUCTION

The formation of ordered phases (superstructures) is a distinguishing feature of strongly nonstoichiometric cubic carbides MC_y with B1-type crystal structure [1]. Carbides are the hardest and high-melting of all known compounds. In the literature, there are limited data on the defragmentation (cleavage, split) of carbide grains (crystallites) to nanocrystalline size during ordering of nonstoichiometric carbides, that is, on the nanostructuring of carbides due to the ordering of carbon atoms at the sites of a nonmetallic face-centered cubic (fcc) sublattice.

The best tool for the simultaneous study of nanostructuring and the ordering of nonstoichiometric carbides is neutron diffraction. On the one hand, the intensities of scattering of neutrons by the nuclei of atoms of transition metals and carbon are comparable in magnitude, which makes it possible to detect the ordering of the light carbon atoms. On the other hand, the diffraction of short-wave neutron radiation makes it possible to determine the size of grains, microstrains and other lattice defects of nanocrystalline substances. Time-of-flight (TOF) diffractometers on pulse neutron sources are the most promising neutron instruments for such studies. Using of a continuous neutron spectrum makes it possible to cover a very wide interval of interplanar distances d_{hkl} and to estimate the effect of different crystal defects (small particle size, microdeformation, nonstoichiometry associated with the presence of vacancies) on the profile and reflection width more accurately than on a conventional diffractometer with a monochromatic neutron beam. Also, TOF neutron diffractometry allows determining the presence in the sample of various fractions with a different particle size.

The first investigations of the effect of nonstoichiometry and small particle size on the microstructure peculiarities of nanocrystalline substances by TOF neutron diffraction analysis were performed only in 2014-2017 on an example of carbides MC_y [2-6].

Niobium carbide NbC_y has a cubic B1-type crystal structure and belongs to the group of strongly nonstoichiometric compounds [1]. Nonstoichiometric niobium carbides NbC_y are used as grain growth inhibitors in hard metals and alloying additives of special steels with increased thermal stability and mechanical strength [7]. According to [1,8,9], when alloying cast iron and steel with vanadium or niobium carbides, nanoscale dispersed carbide particles are released in the metal matrix in the form of a cubic or monoclinic ordered phases.

Fig. 1. The disorder-order phase transformations associated with the formation of the monoclinic (space group C2/m) Nb_6C_5 superstructures in strongly nonstoichiometric cubic (space group Fm3m) niobium carbide NbC_y with the B1 structure
Indeed, according to generalized experimental data [1], ordered monoclinic (space group C2/m) Nb<sub>b</sub>C<sub>y</sub> phase (Fig. 1) is formed in NbC<sub>y</sub> in the composition range from NbC<sub>0.81</sub> to NbC<sub>0.88</sub>.

This investigation is devoted to using the TOF neutron diffractometry method for studying the microstructure peculiarities of coarse-crystalline and nanocrystalline powders of strongly nonstoichiometric cubic (space group Fm-3m) niobium carbides NbC<sub>y</sub> (y = 0.77, 0.84, 0.96) as a function of carbide composition (relative content of carbon, y).

2. EXPERIMENTAL DETAILS

The initial coarse-crystalline powders of nonstoichiometric NbC<sub>y</sub> with the average particle size of 2-3 μm was produced by high-temperature vacuum sintering with following long-time annealing and a slow temperature decreasing from 1300 K to 600 K using the technique described in detail elsewhere [10]. The nanocrystalline carbide powders were prepared by high-energy ball milling of the coarse-crystalline powders in a PM-200 Retsch planetary ball mill for 5, 10, and 15 hours. Ball milling is a simple and efficient method for making various nanocrystalline powders [10]. The milling technique is described in detail in works [10-12].

The coarse-crystalline niobium carbide powders was ground in a PM-200 Retsch ball mill in an automatic mode with the angular speed of rotation ω equal to 8.33 revolutions per second (rps). In all the experiments, the powder charge mass M, i.e. the mass of the initial coarse-crystalline powder, taken for grinding, was 10 g, the ball charge, i.e. the total mass of the grinding balls was ~100 g, and the quantity of grinding balls was ~450 pieces. The volume of the grinding jar (milling bowl) was 50 mL. Grinding jars are intended especially for operation in extreme conditions (long-term grinding at a maximum rotation speed and under high mechanical loadings) and had internal lining with wear-resistant WC – 6 wt.% Co hardmetal based on tungsten carbide with a cobalt binder. The grinding balls of diameter 3 mm were made of the same hardmetal. Isopropyl alcohol (isopropanol) was used as a milling liquid.

According to [11, 12], the dependence of the particle size D of milled powder on its mass M, particle size D<sub>0</sub> of the initial powder, milling duration t and energy of milling E<sub>mill</sub> has the form

\[
D(t, M) = \frac{M[A_0 + B_0 \epsilon(t, M) \ln(D_0 / 2b)]}{E_{\text{mill}}(t) + M[A_0 + B_0 \epsilon(t, M) \ln(D_0 / 2b)] / D_0},
\]

where A<sub>0</sub> and B<sub>0</sub> are constant quantities typical of a given substance and depending on its properties; b is the modulus of the Burgers vector of a given substance, and \( \epsilon \) is micro deformations (microstrains) appearing in the substance during milling.

According to [10], the energy of milling E<sub>mill</sub> with the use of a PM-200 Retsch planetary ball mill is proportional to milling duration t and has the form

\[ E_{\text{mill}} = \kappa \omega^2 t, \]

where \( \kappa \) is a constant coefficient typical of a given ball mill, and \( \omega \) is an angular speed of rotation of the mill in revolution per second. According to [11], the coefficient \( \kappa \) is equal 0.00135 kg·m<sup>2</sup>·s<sup>-1</sup> for a PM-200 Retsch planetary ball mill with mentioned parameters of milling. At this value of \( \kappa \) and \( \omega = 8.33 \) rps, E<sub>mill</sub> = 0.781 t [J]. Thus, the energy E<sub>mill</sub> at milling duration of 5, 10 and 15 h is equal to 14.1, 28.1 and 42.2 kJ, respectively. For the same angular speed of rotation \( \omega \) and the same charged mass M of the initial powder, formula (1) can be written as

\[
D(t) = \frac{[a_0 + b_0 \epsilon(t)] [t + [a_0 + b_0 \epsilon(t)] D_0]},
\]

where, \( a_0 \) and \( b_0 \) are constants. In first approximation it follows from formulas (1, 2) that the particle size D of milled powder is inversely to milling duration t. With an increase in the milling time more than 15 h, D(t) asymptotically tends to certain limiting values. Milling time (milling duration) t for NbC<sub>y</sub> carbide was determined experimentally earlier in work [12].

The specific surface area S<sub>sp</sub> of niobium carbide powders was additionally measured by the BET method on a Gemini VII 2390t Surface Area Analyzer.

The preliminary structural characterization of NbC<sub>y</sub> powders was performed on a Shimadzu XRD-7000 X-ray diffractometer by the Bragg-Brentano method in the angular interval 2θ from 10° to 140° in CuKα1,2 radiation. The X-ray diffraction (XRD) patterns were analyzed using the X’Pert HighScore Plus [13]. The instrumental angular resolution function of the diffractometer. The angular resolution function
3. RESULTS AND DISCUSSION

According to the XRD data, the initial coarse-crystalline niobium carbide powders are single-phase and have the cubic (space group $Fm\overline{3}m$) $B1$-type crystal structure. The quantitative analysis showed that observed broadening of X-ray diffraction reflections is due to both the small size of the coherent scattering regions (CSR) and the presence of microstrains in the carbide nanopowders.

FWHM$_R(2\theta) = (\tan^2 \theta + \tan \theta + w)^{1/2}$ of the Shimadzu XRD-7000 X-ray diffractometer was determined in a special diffraction experiment with the cubic lanthanum hexaboride LaB$_6$ (NIST Standard Reference Powder 660a) having the lattice constant $a = 0.41569162$ nm. This angular resolution function $FWHM_\theta(2\theta)$ has the parameters $u = 0.005791$, $v = -0.004627$ and $w = 0.010201$.

High-resolution neutron diffraction patterns of all samples were recorded at a temperature of 293 K on an HRFD high-resolution time-of-flight Fourier diffractometer (Fig. 2) [14] installing at the channel 5 of the long-pulse IBR-2 reactor (Joint Institute of Nuclear Research, Dubna). In the region of interplanar distances $d_{hkl}$ from $\sim 0.05$ to $\sim 0.50$ nm, the resolution $\Delta d/d$ of this diffractometer is $\sim 0.001$ and is nearly independent of $d_{hkl}$. The resolution function $W_R$ of the HRFD diffractometer was determined with using of Al$_2$O$_3$ standard sample. In the examined interval of interplanar distances $d$ from 0.05 to 0.30 nm, $W_R^2 = (1.66 + 73.8d^2) \times 10^{-8}$ [nm$^2$]. Studied powders were placed in vanadic containers. The neutron diffraction patterns were analyzed according to the Rietveld method using program package FullProf [15].

Fig. 2. Schema of high-resolution time-of-flight Fourier diffractometer

Fig. 3 shows the neutron diffraction patterns of the initial coarse-crystalline NbC$_{0.77}$, NbC$_{0.84}$ and NbC$_{0.96}$ powders, and produced nanopowders recorded on the HRFD diffractometer. Diffraction reflections of nanopowders are strongly broadened owing to ball milling. Besides, the increase of diffuse background is observed. No any superstructure reflections of the ordered monoclinic Nb$_x$C$_y$ phase which appearance, first of all, could be expected in NbC$_{0.84}$ powders, are present on the neutron diffraction patterns of NbC$_y$ powders (Fig. 3).

The quantitative analysis of the neutron diffraction data for niobium carbide nanopowders revealed that the diffraction reflection profiles are described to the best advantage when two cubic (space group $Fm\overline{3}m$) nanopowder fractions with a different lattice constant, different composition and different average particle size are taken into account. Observed diffraction reflections are the sum of the narrow and the broad peaks. Broad peaks correspond to the nanoscale (nanocrystalline) fraction $F_1$, and narrow peaks correspond to the coarse-crystalline $F_2$ fraction.

The lattice constant of the nanocrystalline fraction $F_1$ for all nanopowders decreases slightly with increasing milling duration $t$ (Table 1), and the lattice constant of the coarse-crystalline fraction $F_2$ is almost independent on the milling duration and for nanopowders NbC$_{0.77}$, NbC$_{0.84}$ and NbC$_{0.96}$ is $\sim 0.44388$, $\sim 0.45376$ and $\sim 0.44661$ nm, respectively. It follows from the dependence of the NbC$_y$ lattice constant on the relative carbon content $y$ [1,11,16] that the nanocrystalline and coarse-crystalline fractions of NbC$_{0.77}$ powders have a composition of $\sim$NbC$_{0.78}$ and $\sim$NbC$_{0.79}$, the same fractions of NbC$_{0.84}$ powders have a composition of $\sim$NbC$_{0.80-0.82}$ and...
~NbC\textsubscript{0.825}, and for NbC\textsubscript{0.96} powders the same fractions have a composition of ~NbC\textsubscript{0.84-0.87} and ~NbC\textsubscript{0.95}. The size $D_{CSR}$ of the coherent scattering regions (CSR) in all niobium carbide nanopowders decreases with increasing duration $t$ of milling (Table 1).

Fig. 3. Normalized HRFD neutron diffraction patterns of the initial coarse-crystalline carbide powders NbC\textsubscript{y} and nanopowders produced by milling for 5, 10, and 15 h. Experimental (+) and calculated (——) neutron diffraction patterns are shown. The upper (red) and lower rows of vertical ticks mark the calculated positions of the diffraction reflections for nanocrystalline $F_1$ and coarse-crystalline $F_2$ fractions, respectively. Diffraction reflections for nanocrystalline fraction $F_1$ are displaced into the region of smaller $d$ relative to those of the coarse-crystalline fraction $F_2$. The peaks observed at $d \sim 0.123$, $\sim 0.152$ and $\sim 0.214$ nm are the reflections from vanadic containers.
The smallest particle size $D$ has nanopowders of NbC$_{0.36}$ carbide, which is closest to the stoichiometric composition. The main contribution from 92 to 99% (Table 1) is represented by the broad peaks corresponding to the nanocrystalline fraction $F_1$. With increasing milling time $t$, the content of the nanocrystalline fraction $F_1$ increases, and the content of coarse-crystalline fraction $F_2$ becomes smaller. Thus, two cubic fractions (nanocrystalline fraction $F_1$ and coarse- crystalline fraction $F_2$) coexist in NbC$_y$ nanopowders. Earlier [6, 17], the microheterogeneous structure of NbC$_y$ nanopowders was confirmed by high-resolution electron transmission microscopy (HRTEM). In particles of NbC$_{0.77}$ nanopowder, produced by 5-hour ball milling, separate areas were observed. These areas differ in the mutual orientation, in the observed system of interplanar distances and, more importantly, in the lattice constant values, which are correlated with the $F_1$ and $F_2$ fractions. The micro-regions 10-15 nm in size were assigned to the nanocrystalline fraction $F_1$, and sections with a longer lattice constant were assigned to the coarse-crystalline $F_2$ fraction.

The dependence of the diffraction reflection width $\Delta d$ on the polycrystal interplanar distance $d$ during measurement on an HRFD diffractometer is described [4] as

$$
(\Delta d)^2 = c_1 + c_2 d^2 + c_3 d^3 + c_4 d^4,
$$

where the coefficients $c_1$ and $c_2$ are related to the resolution function and the HRFD diffractometer parameters, $c_3 \approx (2\varepsilon)^2$, $c_4 \approx (k_{\text{av}}/D)^2$, $\varepsilon$ is microstrain, and $D$ is the size of CSR (or, in the first approximation, particle size). The experimental broadening is related to the $\Delta d$ value by the equation $W = K \Delta d$, where the constant for the HRFD diffractometer is $K = 25912.7$, if $\Delta d$ is measured in nm. By substituting $\Delta d$ by $W$ in eq. (3) we have

$$
W^2 = C_1 + C_2 d^2 + C_3 d^3 + C_4 d^4,
$$

(4)

Where, $C_1 = cK^2$, $C_1 + C_3 d^2 = W^2_R$ is a square of resolution function $W_R$ of the diffractometer, and the third and the fourth terms are the contributions from the strain and dimensional broadening. The dependence (4) as a function on $d$ is a parabolic concave curve or straight line, since by definition $C_3 = (2\varepsilon)^2 \geq 0$ and $C_4 = (1/D^4) \geq 0$. But the use of function (4) does not allow explain the convex dependences $W^2(d^2)$ since for them the coefficient $C_4$ must be negative, which is impossible. Convex dependences $W^2(d^2)$ are characteristic for strongly deformed substances [18, 19].

The main origins of the broadening of diffraction reflections are the small particle size $D$ and micro deformations (microstrains) $\varepsilon$ of the crystal lattice owing to its deformation distortions and atomic displacements because of the presence of dislocations. Allowance for the magnitude and anisotropy of micro deformations is especially important in strongly deformed substances [18, 19]. According to [20], in order to describe the experimental data correctly, an additional factor that is responsible for the anisotropy of micro

Table 1. The effect of the milling duration $t$ on the specific surface area $S_{BET}$ of powders, on the content, lattice constant $a$, the size $D_{CSR}$ of coherent scattering region (CSR) and average microstrains $\varepsilon_{\text{aver}} = \Delta a/a$ for nanocrystalline fraction $F_1$ of the NbC$_y$ nanopowders

<table>
<thead>
<tr>
<th>Carbide</th>
<th>$t$ (hour)</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$D_{BET}$ (nm)</th>
<th>Nanocrystalline fraction $F_1$</th>
<th>Lattice constant of coarse-crystalline fraction $F_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbC$_{0.77}$</td>
<td>0</td>
<td>0.282</td>
<td>2730±50</td>
<td>0</td>
<td>0.22</td>
</tr>
<tr>
<td>NbC$_{0.77}$</td>
<td>5</td>
<td>12.44</td>
<td>62±3</td>
<td>93±2</td>
<td>0.4433(2)</td>
</tr>
<tr>
<td>NbC$_{0.77}$</td>
<td>10</td>
<td>18.00</td>
<td>43±3</td>
<td>96±2</td>
<td>0.4434(4)</td>
</tr>
<tr>
<td>NbC$_{0.77}$</td>
<td>15</td>
<td>21.14</td>
<td>36±3</td>
<td>97±2</td>
<td>0.44309(5)</td>
</tr>
<tr>
<td>NbC$_{0.84}$</td>
<td>0</td>
<td>0.155</td>
<td>5020±50</td>
<td>0</td>
<td>0.11</td>
</tr>
<tr>
<td>NbC$_{0.84}$</td>
<td>5</td>
<td>13.74</td>
<td>57±3</td>
<td>93±2</td>
<td>0.44537(1)</td>
</tr>
<tr>
<td>NbC$_{0.84}$</td>
<td>10</td>
<td>20.04</td>
<td>39±3</td>
<td>98±3</td>
<td>0.44528(2)</td>
</tr>
<tr>
<td>NbC$_{0.84}$</td>
<td>15</td>
<td>23.66</td>
<td>33±3</td>
<td>100</td>
<td>0.44555(2)</td>
</tr>
<tr>
<td>NbC$_{0.96}$</td>
<td>0</td>
<td>0.230</td>
<td>350±50</td>
<td>0</td>
<td>0.15</td>
</tr>
<tr>
<td>NbC$_{0.96}$</td>
<td>5</td>
<td>14.22</td>
<td>54±3</td>
<td>95±3</td>
<td>0.44607(1)</td>
</tr>
<tr>
<td>NbC$_{0.96}$</td>
<td>10</td>
<td>20.48</td>
<td>38±3</td>
<td>99±3</td>
<td>0.44607(2)</td>
</tr>
<tr>
<td>NbC$_{0.96}$</td>
<td>15</td>
<td>24.96</td>
<td>31±3</td>
<td>100</td>
<td>0.44588(2)</td>
</tr>
</tbody>
</table>

The effect of the milling duration $t$ on the specific surface area $S_{BET}$ of powders, on the content, lattice constant $a$, the size $D_{CSR}$ of coherent scattering region (CSR) and average microstrains $\varepsilon_{\text{aver}} = \Delta a/a$ for nanocrystalline fraction $F_1$ of the NbC$_y$ nanopowders.
deformations (microstrains), must be considered in the equation (4).

It was shown in study [2] that the broadening \( \beta_{hkl}(2\theta) \) owing to the deformation distortions of the crystal lattice is associated with the anisotropy of these distortions and has the form

\[
\beta_{hkl}(2\theta) = 4k_{hkl}\tan\theta \equiv 4k_{hkl}c_{hkl}^{1/2}\tan\theta = 4k_{hkl}(A + BH)^{1/2}\tan\theta, \tag{5}
\]

where \( \varepsilon_{hkl} = \frac{k_{hkl}}{E_{hkl}} \) is the effective microstrain which is associated with anisotropic Young's modulus \( E_{hkl} \) of a crystal and takes into account the anisotropy of crystal deformation; \( k_{hkl} \) is the constant depending on the density of dislocations in cubic crystals, and \( BH \) is the Burgers vector. According to [21], the coefficient \( C_{hkl} \), taking into account the presence of edge and screw dislocations in cubic crystals, is equal to \( C_{hkl} = A + BH \), where \( A \) and \( B \) are the constants for the given sample depending on the dislocation density and their relative content, and

\[
H = \left( k^2 + l^2 \right) \left( h^2 + k^2 + l^2 \right) \left( h^2 + k^2 + l^2 \right) \]

is the dislocation-related anisotropy contrast factor, which depends on the crystallographic direction \([hkl]\). With allowance for eq.(5), expression (4) can be written as

\[
W^2 = C_1 + C_2d^2 + C_3(A + BH)d^2 + C_4d^4, \tag{6}
\]

Or

\[
\beta^2 = W^2 - W_R^2 = C_3(A + BH)d^2 + C_4d^4 \tag{7}
\]

where \( \beta^2 \) is a square of the broadening with respect to the resolution function \( W_R \). \( C_3 = (2k_{hkl})^2 \) and \( C_4 = 1/D^2 \).

The experimental dependences \( \beta^2(d^2) \) determined for the NbC\(_y\) \((y = 0.77, 0.84, 0.96)\) nanopowders from the HRFD spectra in study [22] are shown in Figure 4. Taking into account measurement and calculation errors, the \( \beta^2(d^2) \) dependences for nanoscale phases of all nanopowders are convex with varying degrees of curvature, which indicates the existing anisotropy of micro deformations. The \( \beta^2(d^2) \) dependences for the coarse-crystalline NbC\(_y\) powders are linear practically and close to the square of the resolution function of the diffractometer, \( W_R^2(d^2) \).

Convex \( \beta^2(d^2) \) dependences are described well by function (7) with a correction for the anisotropy factor \( H \). The calculation showed that the size of CSR of nanopowders NbC\(_y\) \((y = 0.77, 0.84, 0.96)\) decreases with increasing duration \( t \) of milling (see Table 1) and with the approach of NbC\(_y\) carbides to the stoichiometric composition, i.e., with increasing \( y \). Other things being equal, the smallest size of CSR is observed for the nanoscale phase of NbC\(_{0.96}\) carbide.

The average micro deformations \( \varepsilon_{\text{aver}} \) for NbC\(_y\) nanopowders, depending on the carbide composition and the duration \( t \) of milling, vary from \( \sim 0.68 \) to \( \sim 1.43\% \) (Table 2).

Taking into account the anisotropy of the nanocrystalline phase of niobium carbides showed that the largest micro deformation is observed in the direction [222], and the smallest one in the [200] direction, while the micro deformations \( \varepsilon_{200}, \varepsilon_{420}, \) and \( \varepsilon_{422} \) are close to the average micro deformation \( \varepsilon_{\text{aver}} \). Figure 5 as an example shows the distribution of the microdeformations (microstrains) \( \varepsilon_{hkl} \) over the directions \([hkl]\) in the NbC\(_{0.84}\) nanopowder prepared by 10 h milling.

The average value of the \( \varepsilon_{\text{aver}} \) microstrains was found in accordance with [2] as

\[
\varepsilon_{\text{aver}} = \frac{(\Sigma\varepsilon_{hkl}P_{hkl})}{\Sigma P_{hkl}}, \text{ i.e., by averaging the } \varepsilon_{hkl} \text{ taking into consideration the multiplicity factor } P_{hkl}.
\]

### Table 2. Distribution of micro deformations (microstrains) \( \varepsilon_{hkl} \) (%) over the nonequivalent \([hkl]\) directions in the NbC\(_y\) nanopowders produced by milling for 5, 10, and 15 h

<table>
<thead>
<tr>
<th>( hkl )</th>
<th>NbC(_{0.77})</th>
<th>NbC(_{0.84})</th>
<th>NbC(_{0.96})</th>
</tr>
</thead>
<tbody>
<tr>
<td>422</td>
<td>0.73</td>
<td>0.76</td>
<td>1.14</td>
</tr>
<tr>
<td>420</td>
<td>0.65</td>
<td>0.84</td>
<td>1.07</td>
</tr>
<tr>
<td>400</td>
<td>0.49</td>
<td>0.96</td>
<td>0.92</td>
</tr>
<tr>
<td>222</td>
<td>0.79</td>
<td>0.68</td>
<td>1.21</td>
</tr>
<tr>
<td>220</td>
<td>0.73</td>
<td>0.76</td>
<td>1.40</td>
</tr>
<tr>
<td>200</td>
<td>0.49</td>
<td>0.96</td>
<td>0.92</td>
</tr>
</tbody>
</table>
Fig. 4. The experimental dependences $\beta^2(d^2)$ of square of the diffraction reflection broadening, $\beta^2$, for nanocrystalline phases of NbC$_y$ nanopowders ($y = 0.77, 0.84, 0.96$) produced by milling for 5, 10, and 15 h of initial coarse-crystalline powders as a function of the square of the interplanar distance $d^2$ [22]. The width of the reflections was determined with taking into account of correction for the resolution function of the HRFD diffractometer.

Fig. 5. Distribution of microdeformations (microstrains) $\varepsilon_{hkl}$ over the nonequivalent [hkl] directions in the NbC$_{0.84}$ nanopowder prepared by 10 h milling. The radius of the sphere is proportional to the $\varepsilon_{\text{aver}} = 0.014$ (or 1.40 %), the vector length in the [hkl] directions is proportional to $\varepsilon_{hkl}$ values.
The results on $D$ and $d_{002}$ found from the neutron diffraction measurements are in satisfactory agreement with the analogous data obtained by means of X-ray diffraction [11]. However, X-ray diffraction could not detect microinhomogeneity (the presence of fractions differing in particle size) of nanopowders of nonstoichiometric NbC$_y$ carbides.

For the same milling duration $t$, the smallest broadening of the diffraction reflections and the largest CSR size have NbC$_{0.77}$ carbide, which has the greatest hardness. Indeed, according to the data of [1,2,3,24], the microhardness $H_v$ of the NbC$_{0.77}$, NbC$_{0.84}$, and NbC$_{0.96}$ carbides is ~33, ~27 and ~19 GPa.

4. CONCLUSION

A comprehensive analysis of the neutron diffraction data for the NbC$_y$ powders subjected to high-energy milling revealed a rather complex picture of their microstructure.

The study showed that niobium carbide nanopowders have an inhomogeneous fractional composition and contain two cubic fractions with different particle sizes, i.e., they have a bimodal size distribution. The standard diffraction methods, including X-ray diffraction, do not allow one to determine the details of such distribution, which however were established by combined analysis of the profile of all diffraction reflections of niobium carbide nanopowders measured on an HRFD neutron diffractometer. The analysis of the neutron diffraction data revealed micro deformation (microstrain) anisotropy in nanopowders studied. In niobium carbide nanopowders, only disordered phases with different particle sizes and different compositions were observed.

It is clear that a careful control of the milling conditions is necessary in order to produce a nanocrystalline nonstoichiometric carbide powders with a uniform size distribution and the desired composition.

The study of the niobium carbide nanopowders has generally shown that the time-of-flight neutron diffraction technique is promising for studying strongly deformed nonstoichiometric carbide powders. This research shows the advantage of TOF high resolution neutron diffraction. Particularly, an important advantage of TOF high resolution neutron diffraction in comparison with X-ray diffraction is the ability to determine the fractional composition of nanopowders.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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