1. INTRODUCTION

X-ray diffraction or neutron diffraction is one of the main methods for the study of the size of particles and microstrains in nanostructured materials. In a diffraction experiment, the particle size $D$ and microstrain $\varepsilon$ are estimated from the broadening of diffraction reflections. The microstrain depends significantly on the method used for the synthesis of the nanomaterial.

Nanotechnologies related to the preparation of nanostructured materials can be conventionally divided into two groups, namely, the bottom-up and top-down technologies [1–3]. The bottom-up nanotechnologies are mainly based on chemical methods (for example, the sol–gel method and different techniques of synthesis and deposition from aqueous and nonaqueous solutions at low temperatures). Microstrains in materials synthesized by these methods are usually small (0.1–0.2% or less) and have no noticeable influence on their properties.

The preparation of nanomaterials using a top-down nanotechnology is primarily associated with the use of physical methods, among which a special place is occupied by methods based on disintegration of particles (grains) of a material subjected to strong mechanical influences, such as severe plastic deformation and high-energy milling [4–6]. Nanostructured materials synthesized using these methods are characterized by high concentrations of dislocations and large microstrains. Diffraction investigations of the microstructure of such nanomaterials revealed effects caused by the microstrain anisotropy [7–11].

The small size $D$ of grains (crystallites, particles) and the microstrain $\varepsilon$ of the crystal lattice due to deformation distortions and atomic displacements because of the presence of dislocations in the structure of the material are the most known factors responsible for the broadening of diffraction reflections. A less known cause for the broadening of diffraction reflections is an inhomogeneity [12–14], i.e., the inhomogeneity of the composition of the material over the sample volume. The inhomogeneity is possible in compounds and substances with the atomic or atomic–vacancy substitution, for example, in nonstoichiometric compounds $MX_y$ ($MX_y$/$H_17O_4$$_{1-y}$, where $\square$ is the structural vacancy) and solid solutions (alloys) $A_yB_{1-y}$. The inhomogeneity leads to the fact that the composition of a nonstoichiometric compound $MX_y$/$\square$$_{1-y}$ or a solid solution $A_yB_{1-y}$ changes in the interval $y \pm \Delta y$, where $\Delta y > 0$ is the inhomogeneity. Particles (grains) of an inhomogeneous material have different compositions and differ in the lattice parameters, or what is the same, in the interplanar spacings $d \pm \Delta d$. In this case, any reflection is a superposition of reflections from particles (grains) with different interplanar spacings, and, hence, it is broadened.

Until now, the effect of nonstoichiometry and small particle size on specific features of the microstructure of nanocrystalline materials has not been discussed in the literature. This is associated with the
fact that the number of strongly nonstoichiometric compounds (predominantly, superhard cubic carbides and nitrides of Groups IV and V transition metals) is relatively small [14–16], and the preparation of these compounds in the nanometer-scale state is a rather difficult problem.

In this respect, the purpose of the present work was to perform an experimental X-ray diffraction study of the influence of the milling energy, nonstoichiometry, and inhomogeneity on the width of diffraction peaks with the subsequent evaluation of the microstrain anisotropy and particle size. The objects of our investigation were nanocrystalline powders of the nonstoichiometric cubic (space group $Fm\bar{3}m$) tantalum carbide $\text{TaC}_y$ with different relative carbon contents $0.81 \leq y \leq 0.96$, which were prepared by high-energy ball milling of coarse-grained powders.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The initial coarse-grained powders of the nonstoichiometric tantalum carbides $\text{TaC}_{0.81}$, $\text{TaC}_{0.86}$, $\text{TaC}_{0.90}$, and $\text{TaC}_{0.96}$ with the average particle sizes of 2–3 $\mu$m were synthesized earlier in [13] according to the patented method [17]. Details of the synthesis procedure were described in [14–16].

The milling of coarse-grained powders of the nonstoichiometric tantalum carbides was carried out in a PM-200 Retsch planetary ball mill with an angular rotation speed $\omega = 8.333 \text{ rps}$ (500 rpm). In all the experiments, the weight of charging $M$, i.e., the weight of the powder taken for milling, was equal to 10 g, the total weight of milling balls was ~100 g, and the number of milling balls was ~450. The bowl capacity for milling was 50 mL. The milling was performed with the addition of isopropyl alcohol (15 mL). After the milling, the powder was dried. The durations of milling of the initial coarse-grained powders were equal to 5, 10, and 15 h. The milling procedure was described in detail in [6, 18–21].

According to [18, 19], when using a PM-200 Retsch planetary ball mill, the milling energy $E_{\text{mill}}$ has the form

$$E_{\text{mill}} = \kappa \omega^3 t,$$

where $\kappa = 8\pi^3 a_k N_p m (R_c^2 + r^2)^{1/2} R_c (64 - 3(r/R_c))^4/(64 - 16(r/R_c)^2)$ is a constant coefficient that is characteristic of the ball mill with sizes $R_c$ and $r$, $\omega$ is the angular rotation speed of the mill (in revolutions per second), and $t$ is the duration of milling (in seconds). The parameters involved in the formula of the coefficient $\kappa$ for the PM-200 Retsch mill are as follows: $R_c = 0.075 \text{ m}$ is the radius of the circle along which the axis of the bowl moves; $r = 0.0225 \text{ m}$ is the internal radius of the bowl; and $N_p m = 0.1 \text{ kg}$ is the total weight of milling balls, where $N_p$ is the number of milling balls, $m$ is the weight of each ball, and $a_k$ is the efficiency coefficient characterizing the part of the energy consumed for milling of the powder. The coefficient $a_k$ of the PM-200 Retsch mill does not exceed 0.01 [18]. A thorough investigation of the milling of the niobium and tantalum carbides $\text{NbC}_y$ and $\text{TaC}_y$ [21] demonstrated that the efficiency coefficient $a_k$ of the PM-200 Retsch mill is equal to $-0.009$ and, accordingly, we have the coefficient $\kappa \approx 0.00135 \text{ kg m}^2$. For this value of $\kappa$ and the angular rotation speed of the mill $\omega = 8.333 \text{ rps}$, we obtain the parameters $\kappa \omega^3 = 0.781 \text{ J s}^{-1}$ and $E_{\text{mill}} \approx 0.781 t \text{ J}$. Therefore, the milling energies $E_{\text{mill}}$ at the milling times of 5, 10, and 15 h are equal to 14.06, 28.12, and 42.17 kJ respectively.

The specific surface areas $S_{sp}$ of the initial tantalum carbide powders and the same powders after the milling were measured using the Brunauer–Emmett–Teller (BET) method on a Gemini VII 2390t Surface Area Analyzer from the vapor adsorption isotherms of molecular nitrogen at a temperature of 77 K. In the approximation of identical size and spherical shape for all particles, the average particle size $D$ was estimated from the specific surface area $S_{sp}$ according to the formula $D = 6/\rho S_{sp}$ (where $\rho$ is the density of the carbide). The densities of the initial and milled powders of the tantalum carbides $\text{TaC}_{0.81}$, $\text{TaC}_{0.86}$, $\text{TaC}_{0.90}$, and $\text{TaC}_{0.96}$ are presented in the table.

The crystal structure and phase composition of the nonstoichiometric tantalum carbides were determined using X-ray diffraction on a Shimadzu XRD-7000 diffractometer in the Bragg–Brentano geometry within the range of 20 angles from 10° to 140° with a scan step $\Delta(2\theta) = 0.03^\circ$ and an exposure time of 2 s per point in the Cu $K_{\alpha1}$ radiation. The X-ray diffraction patterns were analyzed numerically using the X’Pert Plus software package [22]. The diffraction reflections were described by the pseudo-Voigt function. The average size $\langle D \rangle$ of coherent scattering regions and the microstrains $\varepsilon$ in milled tantalum carbide powders were determined from the broadening of diffraction reflections. To a first approximation, the size of the coherent scattering regions was considered as the average size of particles in the powder.

The broadening of the diffraction reflection $\beta(2\theta)$ was determined as $\beta(2\theta) = [(\text{FWHM}_{\text{exp}})^2 - (\text{FWHM}_{R})^2]^{1/2}$, where $\text{FWHM}_{\text{exp}}$ is the full width of the experimental diffraction reflection at half-maximum and $\text{FWHM}_{R}$ is the instrumental function of the angular resolution of the diffractometer. The resolution function $\text{FWHM}_{R}(2\theta) = (\mu \tan^2 \theta + \nu \tan \theta + \omega)^{1/2}$ of the Shimadzu XRD-7000 X-ray diffractometer was determined in a special diffraction experiment on the cubic lanthanum hexaboride $\text{LaB}_6$ (NIST Standart Reference Powder 660a) with the lattice constant...