

Preparation and structural characterization of nanocrystalline vanadium carbide VC_y powder on the upper boundary of its homogeneity interval

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A nanocrystalline powder of nonstoichiometric vanadium carbide $VC_{0.875}$ with a coherent scattering region of 20 ± 5 nm has been prepared by high-energy ball milling. The crystal structure, microstructure and particle size of the initial and milled powders have been investigated using X-ray diffraction analysis and scanning electron microscopy.

Vanadium carbide is a widely used cubic transition metal carbide. The disordered cubic (space group $Fm\bar{3}m$) vanadium carbide VC_y belongs to strongly nonstoichiometric compounds and has a wide homogeneity interval from $VC_{0.65}$ to $VC_{0.875}$. It forms a V_8C_7 cubic (space group $P4_332$) superstructure and a V_6C_5 superstructure with monoclinic (space groups $C2/c$ or $C2/m$) or trigonal (space group $P3_112$) symmetry.^{1–4} The nanocrystalline powders of vanadium carbide including V_8C_7 have been actively studied.^{5–10}

The initial coarse-grained vanadium carbide $VC_{0.875}$ powder was produced by the carbothermal reduction of V_2O_5 and then subjected to long-term aging at room temperature. According to the chemical analysis data, the aged vanadium carbide contains 18.5 ± 0.1 wt% carbon, including 1.8 ± 0.1 wt% free carbon, and 0.1 wt% oxygen impurity dissolved in the lattice of vanadium carbide. The composition $VC_{0.875}$ corresponds to the upper boundary of the homogeneity interval of the cubic phase with the $B1$ structure.

The initial powder of nonstoichiometric vanadium carbide was ground in a PM-200 Retsch planetary ball mill in an automatic regime at 8.33 rps. The charge M was 10 g, the weight of milling balls was ~ 100 g, and the number of milling balls was ~ 450 . The bowl capacity for milling was 50 ml. The duration t of milling was 15 h. The milling was performed with the addition of isopropanol (5 ml).^{11,12}

The microscopic examination of the initial vanadium carbide powder at a magnification factor of 100 has shown that it contains large agglomerates of irregular shape with an average size of 6–10 μm . However, at a magnification factor of 2000, it is seen that large agglomerates have a complex structure and are a set of a large number of very small particles with a size of ~ 2 –3 μm , which looks like an open flower (Figure 1).[†] The observed crystallites have the shape of curved leaves or petals. As a first

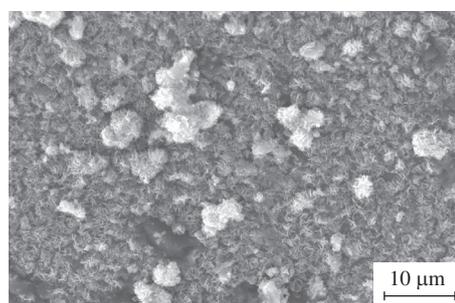


Figure 1 SEM image of the initial coarse-grained powder of $VC_{0.875}$.

approximation, the crystallites can be simulated by a disk with a diameter of 600–800 nm and a thickness of 20–40 nm. Such a microstructure of nonstoichiometric vanadium carbide was experimentally observed and explained by Rempel and Gusev.¹⁴ They showed that the coral-like microstructure of the $VC_{0.875}$ carbide is caused by the disorder-order structural phase transition $VC_{0.875} \rightarrow V_8C_7$, which occurs during the aging of nonstoichiometric carbide and is accompanied by an abrupt change in the lattice constant a_{B1} of the basic phase of the disordered carbide.

The XRD pattern of the initial powder of $VC_{0.875}$ is shown in Figure 2.[†] Along with the structural reflections of the basic cubic phase with the $B1$ structure and the lattice constant $a_{B1} = 416.5$ pm, the XRD pattern exhibits additional weak reflections. The structure refinement of the initial powder of the $VC_{0.875}$ carbide revealed that all the additional reflections are superstructure reflections, which, in their position and intensity, correspond to the cubic ordered phase V_8C_7 with space group $P4_332$. The lattice constant of the ordered phase is 833.2 ± 0.1 pm. The ideal cubic superstructure of the M_8C_7 type with space group $P4_332$ (see lower inset in Figure 2) has a doubled (compared to the disordered basic phase $B1$) lattice constant.^{1–3} Therefore, for the studied vanadium carbide, the lattice constant of the basic phase is $a_{B1} = 416.6$ pm. This value is ~ 0.1 pm larger than the lattice constant of the disordered carbide $VC_{0.875}$. According to published data,^{1,2,4} such a significant difference in the lattice constants of the ordered and disordered $VC_{0.875}$ carbides can be observed when the degree of ordering is close to a maximum value.

Figure 2 shows that all the diffraction reflections of the milled vanadium carbide powder are strongly broadened, as compared to those of the initial coarse-grained powder $VC_{0.875}$. During the milling, a decrease in the particle size, *i.e.*, grinding, is accompanied by the generation of microstrains in the particles. The

[†] The morphology and particle size of the initial and milled powders of $VC_{0.875}$ were examined by scanning electron microscopy (SEM) with a JEOL JSM 6390 LA scanning electron microscope.

The crystal structure and phase composition of $VC_{0.875}$ were determined using X-ray diffraction (XRD) analysis on a Shimadzu XRD-7000 diffractometer in the Bragg–Brentano geometry within a range of 2θ angles from 10° to 140° with a scan step $\Delta(2\theta) = 0.03^\circ$, and high statistics in $CuK\alpha_{1,2}$ radiation. The XRD patterns were analyzed numerically using the X'Pert Plus software package.¹³ The average size $\langle D \rangle$ of the particles [more precisely, the average size of coherent scattering regions (CSR)] in the milled vanadium carbide powder was determined from the broadening of diffraction reflections. The diffraction reflections were described by the pseudo-Voigt function.

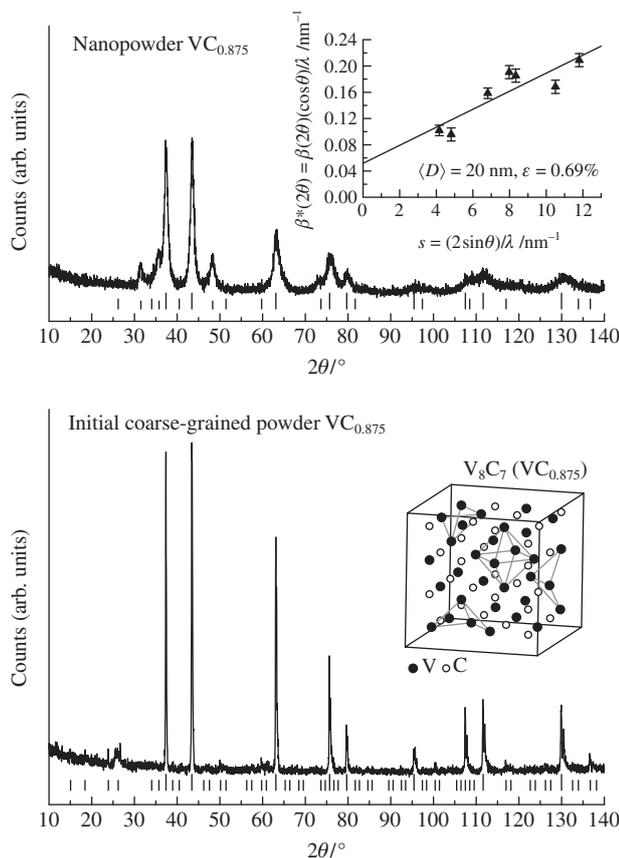


Figure 2 XRD patterns of the initial coarse-grained and milled nanocrystalline powders of $VC_{0.875}$ vanadium carbide. The XRD pattern of the initial vanadium carbide powder, in addition to the structural reflections, contains the superstructure reflections of the ordered cubic (space group $P4_332$) phase V_8C_7 . The XRD pattern of the milled $VC_{0.875}$ powder contains also three reflections from the impurity phase WC. The long and middle ticks correspond to reflections of the disordered cubic (space group $Fm\bar{3}m$) phase $VC_{0.875}$ with the B1 structure and the ordered cubic (space group $P4_332$) phase V_8C_7 , short ticks correspond to reflections of the impurity phase WC, respectively. The upper inset presents the estimate of the average particle size $\langle D \rangle$ and microstrains ε in nanocrystalline $VC_{0.875}$ powder prepared by 15 h high-energy milling: (\blacktriangle) $\langle D \rangle = 20 \pm 5$ nm, $\varepsilon = 0.69 \pm 0.05\%$. The lower inset presents the unit cell of the ordered cubic phase V_8C_7 : vacant (non-filled by carbon atoms) octahedral interstitials of the metallic sublattice are shown.

small (< 200 nm) particle size and microstrains are responsible for the broadening of diffraction reflections. The average particle size $\langle D \rangle$ and the values of microstrains ε in the milled vanadium carbide powders were determined using XRD analysis.

The broadening $\beta(2\theta)$ of the diffraction reflection was determined as $\beta(2\theta) = [(\text{FWHM}_{\text{exp}})^2 - (\text{FWHM}_{\text{R}})^2]^{1/2}$, where FWHM_{exp} is the full width of the experimental diffraction reflection at half-maximum and FWHM_{R} is the instrumental function of the angular resolution of the diffractometer. The resolution function $\text{FWHM}_{\text{R}}(2\theta) = (u \tanh^2 \theta + v \tanh \theta + w)^{1/2}$ of the Shimadzu XRD-7000 diffractometer was determined in a special experiment using cubic lanthanum hexaboride LaB_6 (NIST Standart Reference Powder 660a) with the lattice constant $a = 415.692$ pm; the parameters of this function $u = 0.00616$, $v = -0.00457$ and $w = 0.00778$.

The size and strain broadenings were separated, and the average size $\langle D \rangle$ of the coherent scattering regions and the value of the microstrains ε were found by the Williamson–Hall method^{15–17} using the dependence of the reduced broadening $\beta^*(2\theta) = [\beta(2\theta) \cos \theta] / \lambda$ of the (hkl) reflections on the scattering vector $s = (2 \sin \theta) / \lambda$.

The upper inset in Figure 2 presents the dependences of the reduced broadening $\beta^*(2\theta)$ of the reflections on the scattering

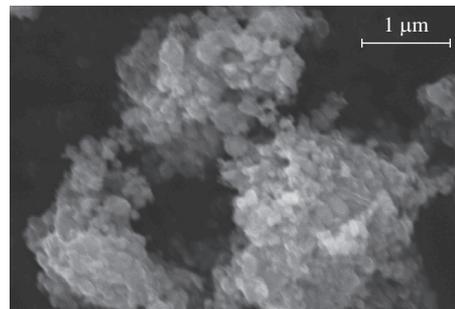


Figure 3 SEM image of nanocrystalline $VC_{0.875}$ powders produced by ball milling within 15 h.

vector s and illustrates the estimation of the average size $\langle D \rangle$ of the coherent scattering regions after the milling of 10 g of $VC_{0.875}$ for 15 h. The analysis of the broadening of diffraction reflections showed that the average size of the coherent scattering regions in the milled vanadium carbide powder is 20 ± 5 nm, and the microstrain ε is 0.0069 ± 0.0005 ($0.69 \pm 0.05\%$).

The results of the electron microscopy investigation of the nanocrystalline vanadium carbide powder obtained by the ball milling are presented in Figure 3. At a magnification factor of 25000, in the milled vanadium carbide powder, the particle size does not exceed 100–150 nm, but the nanoparticles are joined together into large loose agglomerates with a size of 2 μm or greater.

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