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Strain distortions in vanadium carbide $VC_{0.875}$ nanopowders

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The effect of the milling energy of $VC_{0.875}$ carbide on the microstrain anisotropy of nanocrystalline powders has been characterized by the X-ray diffraction analysis; the observed diffraction reflection broadening is caused mainly by the strain broadening rather than the size one.

X-ray or neutron diffraction analysis is the only experimental method for determining lattice microstrains, particle sizes and inhomogeneity as the important microstructure components of nanostructured substances. In diffraction experiments, these characteristics are estimated from the broadening of diffraction reflections.

Many nanostructured materials including nanocrystalline carbide powders are produced by intense plastic deformation and high-energy ball milling.[1,2] The nanostructured materials obtained by these methods feature a large value of microstrains. Diffraction examination of the microstructure of such nanomaterials revealed the effects induced by anisotropy of microstrains.[3–6]

The aim of this work was to perform an experimental X-ray diffraction (XRD) study of the effect of milling energy and inhomogeneity on the diffraction reflection width and subsequent estimation of anisotropy of microstrains. The test materials were the nanocrystalline powders of nonstoichiometric cubic vanadium carbide $VC_{0.875}$ produced by the high-energy ball milling of coarse-grained powder. Nanocrystalline vanadium carbide $VC_{0.875}$ is used as an inhibitor for the growth of grains in hard alloys based on tungsten carbide WC and as an important element of the structure of alloyed steels.[7–10]

The synthesis of the initially coarse-grained $VC_{0.875}$ powder with an average particle size of ~1 μm was described earlier.[11] The powder of $VC_{0.875}$ was milled in a PM-200 Retsch planetary ball mill for 10 and 15 h. The milling procedure was described elsewhere.[1,11–13] The milling energies E_{mill} at milling durations of 10 and 15 h were 28.12 and 42.17 kJ, respectively.

The crystal structure and phase composition of carbide powders were determined on a Shimadzu XRD-7000 diffractometer using $CuK\alpha_{1,2}$ radiation. The diffraction reflection broadening was determined as $\beta(2\theta) = [(FWHM_{exp})^2 - (FWHM_R)^2]^{1/2}$, where $FWHM_{exp}$ is the full width of the experimental diffraction reflection at half-maximum, and $FWHM_R$ is the instrumental angular resolution function of the diffractometer.

If the shape of a diffraction reflection is described by the Lorentz (Cauchy) function, the reduced physical broadening can be found as the sum of size (dimensional), strain and inhomogeneity reduced broadenings[14]

$$\beta^*(2\theta) = \beta_s^*(2\theta) + \beta_d^*(2\theta) + \beta_{hL}^*(2\theta) \equiv$$

$$\equiv 1/D + 2k_\rho(A + BH)^{1/2}s + (k_{hL}/2)s\Delta y, \quad (1)$$

where D is the average particle size; $s = (2\sin\theta)/\lambda$ is the scattering vector; $k_\rho(A + BH)^{1/2} = \varepsilon_{hkl}$ is the effective microstrain and k_ρ, A and B are constants depending on the density of dislocations and their relative content for a given sample;[15] $H = (h^2k^2 + k^2l^2 + h^2l^2)/(h^2 + k^2 + l^2)^2$ is the anisotropy dislocation factor; $(k_{hL}/2)s\Delta y$ is reduced inhomogeneity broadening; $k_{hL} = 4|a'(y)|/a_{B1}(y)$; $a'(y) \equiv da(y)/dy$ is the derivative of the concentration dependence of the lattice constant $a(y)$ of nonstoichiometric compound; and $\Delta y > 0$ is inhomogeneity.

According to the XRD data, the initial vanadium carbide powder is monophase and has a cubic (space group $Fm\bar{3}m$) $B1$ type structure (Figure 1). The degree of homogeneity of the initial coarse-grained $VC_{0.875}$ powder is rather high. This is attested by splitting of $CuK\alpha_{1,2}$ doublets. The first split reflection is the (220) reflection in the region of angles $2\theta = 62.9–63.5°$ (Figure 1). Quantitative estimation of the inhomogeneity of the powder from splitting of (220) reflection[14,16] yields the value $\Delta y = 0.010$. Thus, the composition of vanadium carbide is $VC_{0.875\pm0.010}$.

The effect of milling on the variation of the diffraction reflection profile of vanadium carbide powders is shown in Figure 1. An increase in the duration t and the energy of milling E_{mill} is accompanied by considerable broadening of diffraction reflections.

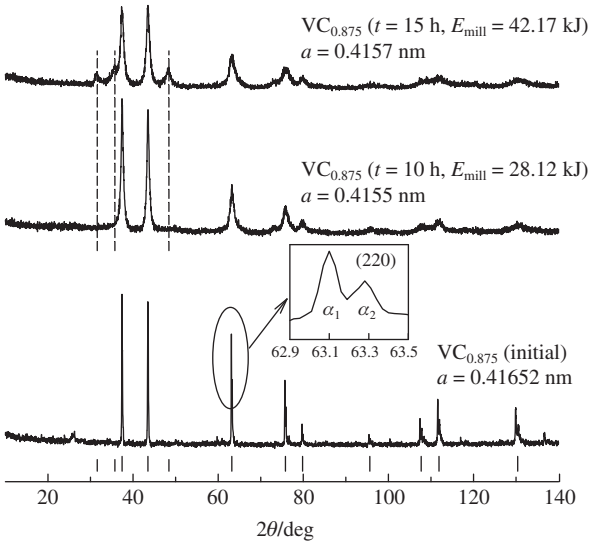

Figure 1 XRD patterns of a coarse-grained powder of vanadium carbide $VC_{0.875}$ and nanocrystalline powders produced by milling for 10 and 15 h with E_{mill} = 28.12 and 42.17 kJ, respectively. The long and short lines correspond to diffraction reflections of $VC_{0.875}$ and hexagonal tungsten carbide WC impurity; the position of WC reflections in the nanopowders is shown by vertical dashed lines.

The nanocrystalline powders produced by milling contained an impurity of ~3.0 wt% tungsten carbide WC (Figure 1). The WC impurity appeared due to the rubbing of grinding balls and the lining of the bowls made of the hard alloy WC–6 wt% Co.

The experimental XRD data demonstrated that the strain broadening is the main contribution to the broadening of diffraction reflections of $VC_{0.875}$ nanopowders. Indeed, the strain broadening $\beta^*_d(2\theta)$ contribution to the observed physical broadening $\beta^*_d(2\theta)$ for any diffraction reflection is >50%.

In the XRD experiment up to 9–10 reflections were detected. With a small number of experimental points, their quantitative description by function (1) with five independent parameters $1/D$, k_ρ, A, B and Δy yields an unstable solution and leads either to a very large (>0.1) or to a negative value of Δy. Both values are physically wrong. Therefore, a correction for inhomogeneous broadening β^*_h with $\Delta y = 0.010$ was introduced into angular broadening. In this case, we consider the function

$$[\beta^*(2\theta) - \beta^*_h(2\theta)] = 1/D + 2\varepsilon_{hkl}s \equiv 1/D + 2k_\rho(A + BH)^{1/2}s, \quad (2)$$

which is minimized for four parameters $1/D$, k_ρ, A and β^*_h.

A rapid reduction of the particle size to 100 nm and less takes place during the first hour of milling. An increase in the duration of milling to 15 h and more is accompanied by a slow asymptotic reduction of the particle size.

The experimental particle sizes D of $VC_{0.875}$ nanopowders determined by the XRD method with and without consideration of anisotropy of microstrains, respectively, are given in Table 1. Determination of nanoparticle size D, based on the XRD data without accounting for microstrains, leads to an underestimation of size D up to 2–3 times. Table 1 shows that the particle size D determination without consideration of the anisotropy of microstrains, *i.e.*, in the assumption of their isotropic distribution, gives underestimated values of D.

Figure 2 demonstrates the distribution of microstrains ε_{hkl} in the nonequivalent directions [*hkl*] in $VC_{0.875}$ nanopowders produced for 10 and 15 h with milling energies E_{mill} of ~28 and ~42 kJ, respectively. The radius of the spheres is proportional to the microstrain ε_{aver} averaged in all the crystallographic directions, and the length of the vectors is proportional to the value of ε_{hkl}. In both nanopowders, the microstrains ε_{111}, ε_{220}, ε_{331} and ε_{422} in the directions [111], [220], [331] and [422] exceed the averaged microstrains ε_{aver} of 0.53 and 0.60% for milling energies of 28 and 42 kJ, respectively. The microstrain ε_{200} is smaller than ε_{aver}, whereas ε_{311} and ε_{420} almost coincide with the averaged microstrain ε_{aver}.

The experimental dependences of the reduced broadening $\beta^*(2\theta)$ of diffraction reflections on the scattering vector s for $VC_{0.875}$ nanopowder produced by milling for 15 h are depicted in Figure 3. The experimental points on the dependence of $\beta^*(2\theta)$ on the scattering vector s plotted without considering the anisotropy

Table 1 Effect of milling time t on the specific surface area S_{sp}, average particle size D and the microstrains ε in nonstoichiometric vanadium carbide $VC_{0.875}$ powders.

t/h	S_{sp}±0.20/ $m^2\ g^{-1}$	D±5/nm				ε_{aver}±0.03 (%)		
		BET[a]	XRD					
			D^b	D^c	D^d	ε^b	ε^c	ε^d
0	1.11	1010	–	–	–	–	–	–
10	28.23	40	18	41	44	0	0.63	0.53
15	33.31	34	9	16	18	0	0.69	0.60

[a]As determined from the Brunauer–Emmett–Teller (BET) specific surface area S_{sp}. [b]As determined in the assumption of the absence of microstrains. [c]As determined in the assumption of isotropic microstrains (without consideration of anisotropy). [d]As determined with consideration for the anisotropy of microstrains ε_{hkl}.

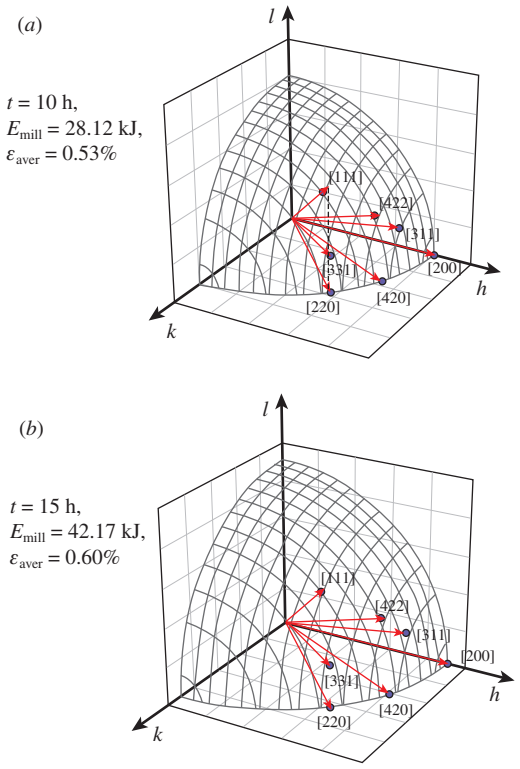

Figure 2 The distribution of microstrains ε_{hkl} in nonequivalent directions [*hkl*] in $VC_{0.875}$ nanopowders produced by milling for (*a*) 10 and (*b*) 15 h. The radius of the sphere is proportional to ε_{aver}; the length of the vectors in the [*hkl*] directions is proportional to ε_{hkl}.

of microstrains are scattered relative to the approximating linear dependence $\beta^*(s)$ [Figure 3(*a*)]. The approximation of the same experimental data by function (2) of $s(A + BH)^{1/2}$ [Figure 3(*b*)] gives better agreement of the experiment with the approximating linear dependence when a correction for inhomogeneous broadening $\beta^*_h(2\theta)$ is introduced and the anisotropy of microstrains is taken into account.

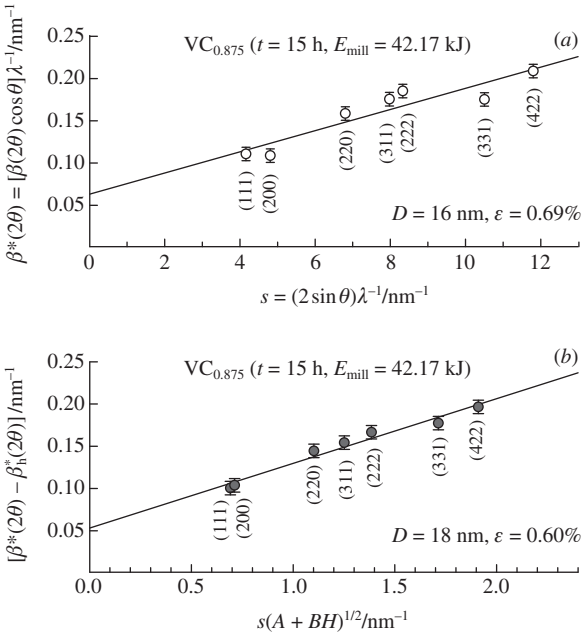

Figure 3 Reduced broadening $\beta^*(2\theta)$ of diffraction reflections of the $VC_{0.875}$ nanopowder produced by 15 h milling: (*a*) the dependence of reduced broadening on the scattering vector s without consideration of anisotropy of microstrains; (*b*) the dependence of reduced broadening with correction for inhomogeneity $[\beta^*(2\theta) - \beta^*_h(2\theta)]$ on $s(A + BH)^{1/2}$ with allowance for anisotropy of microstrains ε_{hkl}.

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