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High-energy milling of nonstoichiometric carbides: Effect of nonstoichiometry on particle size of nanopowders

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ABSTRACT

The dependence between the particle size of milled nanocrystalline powders and the composition of nonstoichiometric compounds within their homogeneity intervals is considered in the framework of the high-energy milling model. It is shown that the effect of nonstoichiometry on the particle size manifests itself in the concentration dependences of the main characteristics (crystal structure parameters, energy of interatomic bonds, elastic and strength properties) of milled nonstoichiometric compounds. Model dependences of the particle size D of nanopowders on the energy of milling proportional to the duration of milling t and on the composition y of nonstoichiometric cubic carbides NbC_y, TiC_y, and VC_y are calculated. The results of these model calculations are compared with the experimental data on $NbC_{0.93}$ and $VC_{0.875}$ milling.

1. Introduction

The last decades saw an active development of different physical material science methods for production of substances and materials in nanocrystalline state. This is connected with the modification of the properties of solid substances when their crystallite (grain, particle) size is reduced to 20–30 nm and under [1–3]. Ball milling is a simple, effective, and productive method for producing different nanocrystalline powders. So far most studies into ball milling of powders have been performed on an empirical level (see for example [4–9]). However, a high-energy milling model appeared recently in the literature [10–15], which establishes a relationship between the particle size of nanopowders and the energy for their milling.

The great majority of solid substances have no homogeneity regions or significant deviations from stoichiometry, therefore the model [11–13,15] is applicable to them without any refinement or additions. However there is a group of strongly stoichiometric compounds with wide homogeneity intervals [16–18]. Strongly nonstoichiometric compounds include in particular cubic and hexagonal carbides, nitrides, and oxides of transitions metals of IV–VI groups. Of special interest are the carbides having the highest hardness and refractoriness among all solid-phase substances. Nonstoichiometric carbides, especially VCy and NbCy, are used as grain growth inhibitors in hardmetals and are important elements of the structure of alloyed steels.

Up to now, the effect of nonstoichiometry on the particle size of nanocrystalline carbide powders produced by any methods including ball milling has not been discussed in the literature.

All properties of nonstoichiometric compounds MX_y and M_2X_y (M = Ti, Zr, Hf, V, Nb, Ta; X = C, N, O) depend on their composition. Therefore in ball milling of powders of nonstoichiometric compounds their characteristics used in the milling model should be represented as functions of the composition (relative content of nonmetal) $y = X/M$.

In this work, the effect of nonstoichiometry on the particle size of powders produced by high-energy ball milling of nonstoichiometric compounds MX_y with a cubic crystal $B1$ structure is considered for the first time. Grinding jars of ball mill had internal lining with WC – 6 wt.% Co hardmetal, the grinding balls were made of the same hardmetal. Transition metal carbides and used WC – 6 wt.% Co hardmetal are comparable on their hardness but wear resistance and also compressive and impact strength of hardmetal is appreciably above. Carbides with different width of the homogeneity intervals, namely titanium, niobium, and vanadium carbides, are chosen for investigation. Cubic titanium and niobium carbides have the broadest homogeneity intervals from $TiC_{0.48–0.50}$ to $TiC_{1.00}$ and from $NbC_{0.70}$ to $NbC_{1.00}$, respectively [17,18]. Stoichiometric carbides $MC_{1.00}$ are the upper homogeneity boundary of the cubic carbides except vanadium carbide. The cubic vanadium carbide has a homogeneity interval from $VC_{0.65}$ to $VC_{0.875}$ and is an interesting

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object since VC_y carbides with $y > 0.875$, stoichiometric carbide $VC_{1.0}$ included, do not exist [16–18].

2. Calculation model

The basic relation of the high-energy milling model [10–15]

$$D(t,M) = \frac{M[A + B\varepsilon(t,M)\ln(D_{in}/2b)]}{E_{mill}(t) + M[A + B\varepsilon(t,M)\ln(D_{in}/2b)]/D_{in}} \quad (1)$$

is a dependence of the particle size D of milled powder on its mass M, milling duration t and energy of milling, E_{mill}. In formula (1), D_{in} is the particle size of the initial powder; $E_{mill}(t) \sim kt$ is the energy of milling proportional to the duration of milling (the coefficient k in the energy $E_{mill}(t)$ depends on the design of the milling plant and the mechanics of grinding bodies); ε is microstrains appearing in the substance during milling; $A = \frac{f_s}{f_v}\frac{qu}{s_f d}$ and $B = \frac{f_s}{f_v}\frac{\beta G b\sqrt{3C}}{12\pi(1-\nu)d}$ are certain constants typical of a given substance and depending on its properties; $b = |\mathbf{b}|$ is the modulus of the Burgers vector; d, G, and ν are the density, shear modulus, and Poisson coefficient of milled substance; q/s_f is the number of interatomic bonds passing through the slip plane with area s_f falling on one unit cell of considered crystal; u is the energy of an individual interatomic bond of milled substance; $f_s/f_v = 6$ is the relation of the particle volume and surface area form factors; $C = 18$ is the coefficient relating the density of dislocations to the value of microstrains [19]; and $\beta = 100$ is the coefficient allowing for additional energy consumption for deformation of the milling plant and grinding bodies. It is easy to see that formula (1) meets the edge condition $D(0,M) = D_{in}$ since in the initial time $t = 0$ the energy of milling $E_{mill}(0) = 0$ and microstrains $\varepsilon(0,M) = 0$. The milling duration (or milling time) t is the most important parameter. Usually the time t is so chosen as to achieve a stable equilibrium between the fracturing and cold welding of the powder particles. The time required vary depending on the design of the mill used, the mass ball-to-powder ratio, and the temperature of milling.

From formula (1) and the explicit form of coefficients A and B it follows that milling of a substance with a higher density d, all other factors being the same, gives rise to a powder with a smaller particle size. Indeed, a substance with a higher density takes a smaller volume V, therefore the specific energy of milling E_{mill}/V is greater, and at an equal mass M and the same energy E_{mill} the milled powder should have particles of a smaller size. Let us compare the results obtained in different works for coarse-grained powders of substances (tungsten and vanadium carbides WC and $VC_{0.875}$ and vanadium monoxide $VO_{1.00}$) ground in a PM-200 Retsch mill under equal conditions (angular speed of rotation $\omega = 8.33$ rps, powder mass $M = 0.01$ kg, total mass of grinding balls ~0.1 kg). The densities of WC, $VC_{0.875}$, and $VO_{1.00}$ are 15.8, 5.36, and 5.49 g cm^{-3}, respectively. For example, milling of hexagonal tungsten carbide WC for 1, 3, and 10 h resulted in nanopowders with the average particle size of 70 ± 10, 40 ± 10, and 20 ± 5 nm, respectively [11,15]. According to scanning electron microscopy data, the average particle size of cubic vanadium monoxide VO ($V_{0.82}O_{0.82}$) powder produced by 4 h milling was ~100–120 nm [9]. Nanocrystalline powder of cubic vanadium carbide $VC_{0.875}$ milled for 3 and 10 h had the average particle size of ~100 ± 10 and ~60 ± 10 nm, respectively [20]. From these data it is clear that at comparable milling conditions, powders with smaller particles are prepared from substances having higher densities.

Since all properties of nonstoichiometric compounds MX_y depend on their composition, the characteristics of a compound MX_y, which explicitly or implicitly enter into formula (1), should be represented as functions of the relative content of nonmetal $y = X/M$ in order to take into consideration the effect of nonstoichiometry on the particle size of milled compound. These are the main characteristics such as the lattice constant a_{B1}, atomization energy E_{at}, shear modulus G, and Poisson coefficient ν. The length of the Burgers vector b and the density d are related with the lattice constant a_{B1}; the number q of interatomic bonds passing through the slip plane of considered crystal and the energy u of an individual interatomic bond can be expressed knowing the crystal structure of the examined compound and its atomization energy. As a result, formula (1) takes the form

$$D(y,t,M) = \frac{M\{A(y) + B(y)\varepsilon(y,t,M)\ln[D_{in}/2b(y)]\}}{E_{mill}(t) + M\{A(y) + B(y)\varepsilon(y,t,M)\ln[D_{in}/2b(y)]\}/D_{in}}. \quad (2)$$

Let us consider how nonstoichiometry is taken into account using cubic carbides MC_y as an example.

For this purpose at first we will find quantitative dependences of the atomization energy, the lattice constant and the shear modulus on the composition of some nonstoichiometric cubic carbides.

2.1. Atomization energy

According to [11–13,15], the energy u of an individual interatomic bond can be estimated from the atomization energy E_{at}. In case of cubic carbides MC_y with a $B1$ structure, the unit cell contains 4 formula units MC_y, therefore for one cell there is an energy of $4E_{at}/N_A$, where $E_{at}(y)$ is the carbide atomization energy and $N_A = 6.023 \times 10^{23}$ mol^{-1} is the Avogadro number. One unit cell of carbides with a $B1$ structure includes 24 paired bonds M—C with a distance between M and C atoms equal to $a_{B1}/2$. So the energy u of one interatomic bond is $E_{at}(y)/6N_A$.

In cubic carbides, the motion of dislocations occurs mainly by the slip system {1 1 1} ⟨1 1 0⟩ [21–23], i.e. along the {1 1 1} planes in the direction ⟨1 1 0⟩. Slippage of close-packed atomic planes in the ⟨1 1 0⟩ direction corresponds to the Burgers vector b with the length $b = a_{B1}\sqrt{2}/2$. In [24] it is shown that within a cubic unit cell the slip plane {1 1 1} passing through the middle of M—C bonds has an area of $s_f = (3\sqrt{3}/4)a_{B1}^2$ and crosses nine M—C bonds (Fig. 1), that is why in case of deformation along this plane $q/s_f = 4\sqrt{3}/a_{B1}^2(y)$. Therefore $qu/s_f = (2\sqrt{3})E_{at}(y)/[3N_A a_{B1}^2(y)]$. The density of the cubic carbide MC_y is $d(y) = 4M_{MC_y}/N_A a_{B1}^3(y)$, where

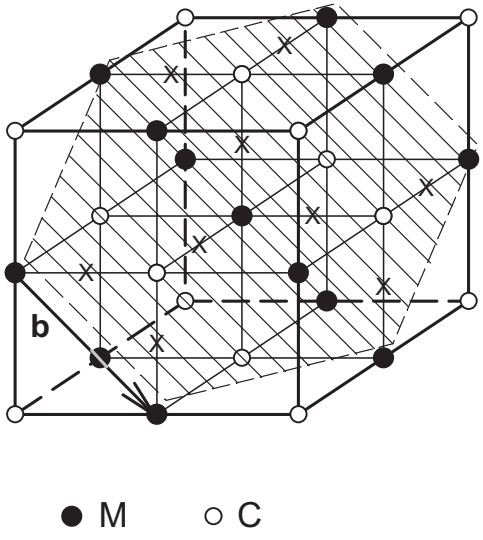

Fig. 1. The slip system {1 1 1} ⟨1 1 0⟩ in nonstoichiometric carbides MC_y with the basis $B1$ type cubic structure. During slipping in the {1 1 1} plane, nine M—C bonds are disrupted: (×) are the cross points of paired bonds M—C by the slip plane, $\mathbf{b} = \langle 1\,1\,0\rangle/2$ is the Burgers vector showing the direction of slipping in the {1 1 1} plane.