Int. Journal of Refractory Metals and Hard Materials 51 (2015) 70–80

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

Anisotropy of strain distortions in nanopowders of nonstoichiometric vanadium and tantalum carbides

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ARTICLE INFO

Article history:
Received 5 December 2014
Received in revised form 25 February 2015
Accepted 3 March 2015
Available online 6 March 2015

Keywords:
Vanadium carbide
Tantalum carbide
Nonstoichiometry
Inhomogeneity
Nanopowders
Anisotropy of microstrains
Particle size

ABSTRACT

For the first time, the effect of milling energy and nonstoichiometry of vanadium carbide $VC_{0.875}$ and tantalum carbide TaC_y ($0.81 \le y \le 0.96$) on microstrains anisotropy and the particle size of nanocrystalline powders has been studied experimentally by the X-ray diffraction method. A functional dependence of reduced broadening of diffraction reflections on the scattering vector has been obtained, which takes into consideration the contributions from size, strain and inhomogeneity broadenings. The average size of coherent scattering regions and the value of microstrains in crystallites accounting for anisotropy of strain distortions have been estimated. It is shown that allowance for anisotropy of microstrains and inhomogeneity broadening gives more accurate description of the experimental results on diffraction reflection broadening and more accurate determination of the nanoparticle size.

1. Introduction

Compounds of IV–VI group transition metals with carbon or nitrogen, MX_y, have wide homogeneity intervals and belong to the group of strongly nonstoichiometric interstitial compounds [1–3]. Strongly nonstoichiometric interstitial compounds and their solid solutions are the hardest and most refractory substances that we know. The content of structural vacancies in the nonmetal sublattice of these compounds may amount to 30–50 at.% at the lower boundary of the homogeneity region. Owing to the large concentration of structural vacancies, they possess radiation stability [4]. The high concentration of structural vacancies is a prerequisite of wide-spread ordering of nonstoichiometric compounds [3,5–14], which is accompanied by modification of the crystal structure, microstructure and all properties. In modern engineering, these materials are used for the production of structural and tool materials capable of working at high temperatures, in aggressive media and under high loads, etc.

In the recent twenty years, nonstoichiometric compounds, especially carbides and carbide solid solutions, are actively produced, studied and employed in nanocrystalline state [15–18]. The microstructure of nanocrystalline substances differs noticeably from that of coarse-grained compounds [19–22]. The most important components of the microstructure of nanostructured substances are the particle (grain) size and lattice microstrains.

Vanadium, niobium and tantalum carbides are the most extensively used cubic carbides of transition metals. They are applied as grain growth inhibitors in hard alloys based on tungsten carbide. During sintering of nanostructured tungsten carbide based hard alloys with additions of nanocrystalline carbide powders VC_y, NbC_y and TaC_y, it is necessary to take into account the presence and space distribution (anisotropy) of microstrains in the nanopowders to provide the homogeneity of sintered hard alloys [18,23]. According to [23], abnormal grain growth occurred with a high microstrain introduced through milling. The conditions of annealing of microstrains depend on their value and anisotropy.

Vanadium carbide $VC_{0.875}$ is used also as an important element of the structure of alloyed steels. The mechanical properties of such steels depend on the form of disperse carbide precipitates. According to [24,25], during alloying of cast iron and steels with carbide $VC_{0.875}$, disperse carbide particles are precipitated in the form of ordered phase V_8C_7. The size of the disperse precipitates depends on the value of microstrains in them.

X-ray and neutron diffraction is the only method for the determination of microstrains as an important component of the microstructure of nanostructured substances. It allows one to determine simultaneously the particle size and the inhomogeneity of substance, which cannot be achieved by any other experimental techniques including electron microscopy.

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http://dx.doi.org/10.1016/j.ijrmhm.2015.03.003
0263-4368/

In diffraction experiment, the particle size D and the value of microstrains ε are estimated from the broadening of diffraction reflections. The value of microstrains depends appreciably on the method of production of nanomaterial.

The nanotechnologies for the production of nanostructured materials are conventionally divided into two groups: bottom-up and top-down [26–28]. The bottom-up technologies are based mainly on chemical methods including the sol–gel technique and different methods of synthesis and deposition from aqueous and non-aqueous solutions at low temperatures. The microstrains in the substances produced by these methods are usually small (0.1–0.2% and lower) and exert almost no effect on the properties.

The production of nanostructured materials by top-down nanotechnologies is connected mainly with the use of physical methods. Among them, the methods, in which particles (grains) are milled as a result of strong mechanical action, such as intensive plastic deformation and high-energy milling, occupy a special place [15,29,30]. The nanostructured materials produced by these methods feature a high concentration of dislocations and a large value of microstrains. Diffraction examination of the microstructure of such nanomaterials revealed the effects induced by anisotropy of microstrains [31–35].

Small grain (crystallite, particle) size D and microstrains ε of the crystal lattice caused by its strain distortions and by displacements of atoms owing to the presence of dislocations are the most familiar reasons of diffraction reflection broadening. The less known reason is inhomogeneity [6,36,37], i.e. heterogeneity (nonuniformity) of the composition of a substance over its volume. Inhomogeneity is possible in compounds and substances with atomic or atomic-vacancy substitution: in nonstoichiometric compounds MX_y ($MX_y\square_{1-y}$, where X = C, N, O, and □ is a structural vacancy) and solid solutions (alloys) A_yB_{1-y}. In the presence of inhomogeneity, the composition of nonstoichiometric compound MX_y or solid solution A_yB_{1-y} varies in the interval $y \pm \Delta y$, where $\Delta y > 0$ is inhomogeneity. The particles (grains) of inhomogeneous nonstoichiometric compound have different compositions and, consequently, differ from one another by the value of interplanar distances $d \pm \Delta d$ and lattice constants. In this case, any reflection is a superposition of diffraction reflections from particles (grains) with different interplanar distances and therefore a reflection is broadened (Fig. 1).

Up to now, the effect of nonstoichiometry and small particle size on the peculiarities of the microstructure of nanocrystalline substances has never been discussed in the literature. This has to do with the circumstance that the number of strongly stoichiometric compounds (mainly superhard cubic carbides and nitrides of IV and V group transition metals) is small [3,5,6] and their production in the nanocrystalline state is rather difficult.

In this connection the aim of the present work is experimental X-ray diffraction (XRD) study of the effect of milling energy, nonstoichiometry and inhomogeneity on the diffraction reflection width and subsequent estimation of anisotropy of microstrains and particle size. The objects of investigation are nanocrystalline powders of nonstoichiometric cubic (space group $Fm\bar{3}m$) vanadium carbide $VC_{0.875}$ and tantalum carbide TaC_y with different relative contents of carbon, $0.81 \le y \le 0.96$, produced by high-energy milling of coarse-grained powders.

2. Samples and experimental techniques

The initial coarse-grained powders of nonstoichiometric vanadium carbide $VC_{0.875}$ and tantalum carbides $TaC_{0.81}$, $TaC_{0.86}$, $TaC_{0.90}$ and $TaC_{0.96}$ with the average particle size of 1–3 μm were produced by us with using the patented technique [38]. The method of synthesis is described in detail in [3,5,6].

Coarse-grained powders of nonstoichiometric vanadium and tantalum carbides were milled in a PM-200 Retsch planetary ball mill with the angular rate of rotation $\omega = 8.333$ rps. In all the experiments, the charge mass M, i.e. the mass of the powder to be milled, was 10 g, the total mass of grinding balls was ~100 g and the number of grinding balls was ~450. The volume of the milling cup was 50 ml. During milling, 15 ml of isopropyl alcohol was added, and after milling the powder was dried. The duration of milling of initial coarse-grained powders was 5, 10 or 15 h. The milling procedure is described in detail elsewhere [15, 39–42].

According to [39,40], the energy of milling E_{mill} with the use of a PM-200 Retsch planetary ball mill has a form of

$$E_{\text{mill}} = \kappa\omega^3 t, \tag{1}$$

where $\kappa = 8\pi^3 a_k N_b m\left(R_c^2 + r^2\right)^{1/2} R_c \frac{64-3(r/R_c)^4}{64-16(r/R_c)^2}$ is a constant coefficient typical of a mill with sizes R_c and r; ω is an angular rate of rotation of the mill in revolution per second; and t is the duration of milling in seconds. For a PM-200 Retsch mill, the parameters entering into the coefficient κ have the following values: $R_c = 0.075$ m is the radius of the circle, round which the axis of the cup moves; $r = 0.0225$ m is the inner radius of the cup; the total mass of grinding balls is $N_b m = 0.1$ kg, where N_b is

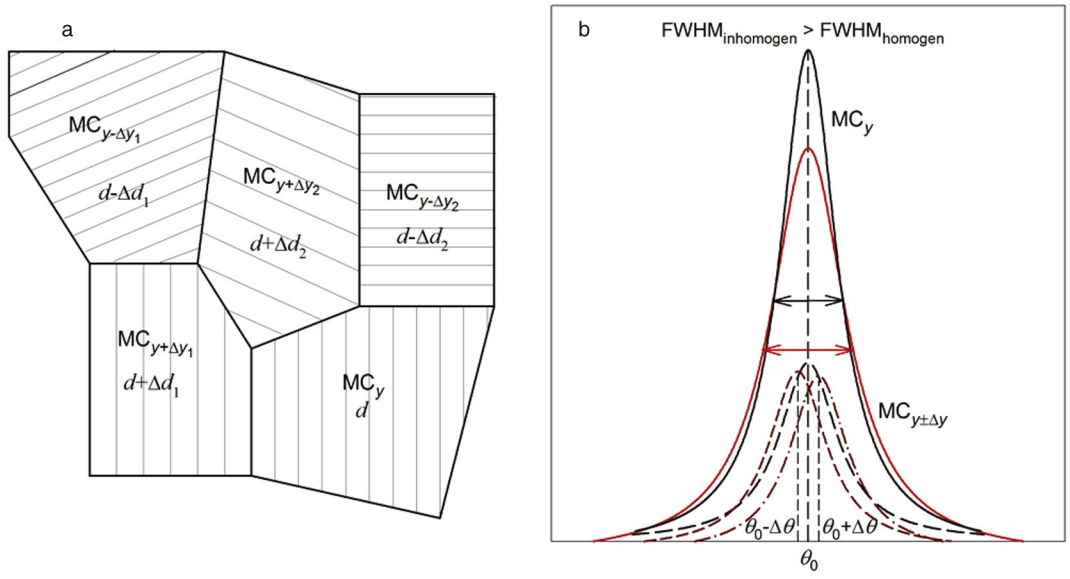

Fig. 1. The model of inhomogeneous broadening: (*a*) grains of inhomogeneous nonstoichiometric carbide MC_y have different compositions and differ from one another by the value of interplanar distances $d \pm \Delta d$; (*b*) in this case any reflection is a superposition of diffraction reflections from grains with different interplanar distances and therefore broadens.