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Nanocrystalline ordered vanadium carbide: Superlattice and nanostructure

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ABSTRACT

The crystal structure, micro- and nanostructure of coarse- and nanocrystalline powders of ordered vanadium carbide V_8C_7 have been examined by X-ray and neutron diffraction and electron microscopy methods. The synthesized coarse-crystalline powder of ordered vanadium carbide has flower-like morphology. It was established that the real ordered phase has the composition $V_8C_{7-\delta}$ ($\delta \cong 0.03$) deviating from perfect stoichiometric composition V_8C_7. The vanadium atoms forming the octahedral environment $\square V_6$ of vacant sites in $V_8C_{7-\delta}$ are displaced towards the vacancy $\square$. The presence of carbon onion-like structures was found in the vanadium carbide powders with a small content of free (uncombined) carbon. The nanopowders of $V_8C_{7-\delta}$ carbide with average particle size of 20–30 nm produced by high-energy milling of coarse-crystalline powder retain the crystal structure of the initial powder, but differ in the lattice deformation distortion anisotropy.

1. Introduction

Vanadium carbide is one of the most commonly used cubic carbides of transition metals. It is employed as a grain growth inhibitor in hardmetals and as an important structural component of alloyed steels widely applied in the production of aircraft and automobile engines.

Disordered cubic vanadium carbide VC_y with *B*1-type structure belongs to the group of strongly nonstoichiometric compounds [1] and has wide homogeneity intervals: From $VC_{0.72}$ to $VC_{0.875}$ at 1500 K and from $VC_{0.60}$ to $VC_{0.88}$ at ~2450 K [2]. Carbides $MC_{1.0}$ are the upper boundary of the homogeneity interval of nonstoichiometric cubic carbides MC_y except vanadium carbide. The cubic carbide VC_y has the upper boundary of the homogeneity interval at the composition $VC_{0.875}$, which is rather far from the stoichiometric composition $MC_{1.0}$.

Under thermodynamic equilibrium, nonstoichiometric carbides can be in disordered or ordered state [1]. In nonstoichiometric cubic vanadium carbide VC_y, ordered phases of the type V_3C_2, V_6C_5 and V_8C_7 can be formed [2]. The phase V_8C_7 was found only in vanadium carbide VC_y and it is not observed in carbides of other transition metals; its existence is connected with a specific position of the upper boundary of the homogeneity interval of vanadium monocarbide at $VC_{0.875}$. The ordered phase V_8C_7 is formed rather easily during high-temperature sintering of vanadium and carbon or during reduction of

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vanadium oxide by carbon in the process of subsequent slow cooling of synthesized vanadium carbide from synthesis temperature to room temperature [1].

The V_8C_7 superlattice was first observed experimentally by X-ray diffraction (XRD) and nuclear magnetic reconance methods [3–5]. The authors [3,4] showed that the phase V_8C_7 has cubic symmetry and belongs to the space group $P4_332$. The neutron diffraction investigations of the $VC_{0.865}$ carbide at a temperature of 4.2 and 300 K [7] confirmed the existence of the V_8C_7 phase and its cubic symmetry. According to [6], the carbon atoms in the unit cell of V_8C_7 phase are not virtually displaced from the perfect lattice positions. However, the studies [5,7,8] of the V_8C_7 phase revealed large displacements of the V atoms towards the vacant site □ of the nonmetal sublattice and even greater displacements of the C atoms. The estimates of the atomic displacement values made from the neutron diffraction results [6,9] and XRD data [8,10] differ considerably.

According to [11,12], alloying of cast iron and steels with vanadium carbide gives rise to nanosized disperse carbide particles in the form of ordered phases V_8C_7 or V_6C_5. Vanadium carbide used as a grain growth inhibitor in hardmetals based on tungsten carbide WC is formed as nanosized films or nanoparticles [13,14].

Methods for the production of substances in the nanostructured state have been developed in the latest decades. The disordered carbides MC_y with cubic $B1$ type structure contain up to 30–50% structural vacancies □ in the nonmetal sublattice [1,15]. Below 1300 K, the $B1$ structure becomes unstable and disorder-order phase transitions take place in nonstoichiometric carbides resulting in the formation of ordered phases with complex superlattices [1,16,17]. Order-disorder and disorder-order transformations in carbides are first-order phase transitions with a discontinuous variation of volume at the disorder-order transformation temperature T_{trans} [1,14,17]. The differences in the lattice parameters of the disordered and ordered phases in the sample induce stresses leading to cracking of crystallites at the disordered-ordered phase interface. By controlling the sizes of the ordered phase domains, it is possible to produce nanostructured nonstoichiometric carbides [18,19].

The idea of formation of a nanostructure by atomic-vacancy ordering of nonstoichiometric compounds was implemented for the first time on the example of nonstoichiometric vanadium carbide [20]. Vanadium carbide $VC_{0.875}$ was the first carbide, in which nanostructure was created as a result of disorder-order transformation $VC_{0.875} \rightarrow V_8C_7$ both in coarse-grained powder [20] and in bulk carbide [10].

Until recently, all the investigations of crystal structure of nanocrystalline nonstoichiometric substances available in the literature were performed only by means of the XRD method. There is no mentioning of neutron diffraction analysis even in the latest review [21] of diffraction analysis methods for nanocrystalline substances. Only lately, time-of-flight (TOF) neutron diffraction analysis [22] was used for the first time to examine the peculiarities of microstructure of nanocrystalline nonstoichiometric niobium carbide $NbC_{0.93}$ [23,24]. This is astonishing, as neutron TOF diffractometers operational on pulsed sources have a great potential for the characterization of the microstructure of fine-grained materials. Their resolution function, in fact, is almost independent of scattering vector Q within a fairly wide range. This is certainly quite different from the conventional neutron diffractometers using a monochromatic beam where the resolution function $R(Q)$ is usually parabolic with a rapid rise in the range of small Q values. In addition, the application of correlation Fourier technique on pulsed neutron source and the realization of the so-called reverse time-of-flight (RTOF) data acquisition method make it possible to achieve very high resolution comparable with that of X-ray instrument while maintaining the short source-to-detector distance and, consequently, the high brightness. The resolution of RTOF diffractometer mostly depends on the maximum rotation speed of the Fourier chopper, and can be turned for specific purposes. Diffraction peaks obtained on such an instrument should be symmetric, without long “tails” observed on diffraction spectra from conventional TOF instruments, installed at spallation neutron sources. This fact greatly simplifies precise peak profile analysis [24].

Ordering in nonstoichiometric vanadium carbide is connected with redistribution of carbon atoms C and structural vacancies □ in the nonmetal sublattice sites. Although the crystal structure of the ordered phase V_8C_7 in coarse-grained bulk samples has been studied in sufficient detail, the information about atomic displacements is contradictory. Until now it is not known whether V_8C_7 has at least a narrow homogeneity interval or not at all. For nanocrystalline vanadium carbide, this is not known either. Moreover, it is not clear even if the V_8C_7 superstructure is retained in nanocrystalline powders with medium-sized particles of 20–30 nm or less. This can be elucidated with the use of neutron diffraction analysis together with XRD and high-resolution transmission electron microscopy (HRTEM).

Among neutron tools, TOF diffractometers on pulse neutron sources [22] hold most promise for such studies. The use of a continuous wavelength neutron spectrum makes it possible to cover a very wide interval of interplanar distances d_{hkl} (from ~0.05 up to ~1.5 nm and more). It is also important that the resolution of the TOF-diffractometer depends very weakly on d_{hkl} value.

In this work, X-ray diffraction, TOF-neutron diffraction analysis, high-resolution scanning and transmission electron microscopy were used for the first time to examine experimentally the crystal structure and microstructure of dispersed nanocrystalline carbide V_8C_7 produced by high-energy ball milling of coarse-grained powder of the ordered phase V_8C_7. The coarse-grained powder of V_8C_7 was also studied for comparison.

2. Experimental details

The initial powder-like vanadium carbide $VC_{0.875}$ was obtained by carbothermal reduction of the oxide V_2O_3 with carbon by the reaction $V_2O_3 + mC \rightarrow 2VC_{0.875} + 3CO$ in Ar atmosphere at 1570 K and then it was exposed to long-term aging at room temperature. The reduction of V_2O_3 by carbon in the amount of $m = 4.75$ corresponding to reaction stoichiometry resulted in the formation of a two-phase product containing the cubic carbide VC_y with an admixture of the lower hexagonal carbide V_2C.