Room-Temperature Synthesis of the TiC, ZrC, HfC, VC, NbC and TaC Powder Monocarbides

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The nanoscaled (up to 30 nm) TiC, ZrC, HfC, VC, NbC and TaC monocarbides with NaCl-type structure have been synthesized from the elemental metals and the carbon nanotubes (CNTs) by mechanical alloying in a high energy planetary ball mill in an argon atmosphere. The powders obtained were examined by X-ray diffraction method. It is shown that mechanical alloying is accompanied by a decrease in the lattice parameters of MeC carbides formed and by a decrease of the total number of atoms in their crystal structure, i.e. by an increase of structural vacancies in the materials obtained. On the whole, monocarbides obtained can be arranged by the simplicity of their formation in a ball mill as: HfC → ZrC → TiC → TaC → NbC → VC.

Introduction

Due to a high melting temperature, extraordinary hardness and toughness combined with good electrical and thermal conductivity as well as excellent resistance to wear and abrasion, metal carbides are known to be widely used in some industrial applications as reinforcement additions for composite materials and for functional coatings improving the sharpness of cutting edges. The synthesis of the MeC refractory monocarbides (where Me are IVb and Vb transition metals) is usually performed at high-temperature (1300 – 2300

°C) processes such as direct reaction either by the melting or sintering of pure metals or metal hydrides; direct reaction of metal oxides and excess carbon in a protective or reducing atmosphere; reaction of metal with a carburizing gas; or precipitation from the gas phase by reacting the metal halide or metal carbonyl in hydrogen [1, 2].

However, mechanical alloying (MA) allows us to produce a variety of commercially useful and scientifically interesting materials through the high-energy ball-milling technique. Along with the fact that the process takes place

at room temperature, the main advantages of MA are the simple technical opportunity of the process performance and the advanced features of the nanoscaled materials obtained. Previously the Matteazzi, Teresiak et al. [3, 4] have successfully provided the direct room-temperature synthesis of the TiC, ZrC, HfC, VC, NbC and TaC monocarbides (the grain size of 7-20 nm) by milling the metal powder and carbon in a form of graphite. Besides, it was shown that both milling atmosphere and different carbon sources (graphite, activated carbon, carbon fibers or carbon nanotubes) have an effect on mechanism of synthesis and change the reaction rate in a case of TiC formation [5–7]. Moreover, the remarkable thing is that CNTs could considerably accelerate the course of Ti–C reaction [6]. Our previous studies have also proved this conclusion [8, 9]. So, the substitution of graphite for CNTs in the Fe₃C, WC and Mo₂C carbides fabrication drastically cuts the processing time and makes synthesis more productive.

In this paper we present the results of our study of the *MeC* (Me is Ti, Zr, Hf, V, Nb or Ta) monocarbides obtained by mechanical alloying of the elemental *Me*-CNTs blend in a high-energy ball mill. The morphology, crystal and real structure of the monocarbides obtained are analyzed.

Experimental part

Elemental metals (~99.6% purity, weight content of 5 g) and multiwall CNTs were mixed to give the desired average composition and sealed in a vial under an argon atmosphere. Both metal powder and calibrated metal filings were used as raw metal materials for mechanical alloying (Table 1). Multiwall carbon nanotubes used in this study were synthesized by the catalytic chemical vapor deposition method (CVD) at TM Spetzmash Ltd (Kyiv, Ukraine). Parameters of CNTs are as follows: the average diameter is (10 – 20) nm, the specific surface area (determined by argon desorption method) is (200 – 400) m²/g and their poured bulk density varies from 20 to 40 g/dm³. Hardened stainless steel vial (70 mm height, 50 mm diameter) and balls (11 units of 15 mm diameter) with a ball-to-powder weight ratio of 40:1 were used. The milling process carried out in a high energy planetary ball mill (the rotation speed of 1480 rpm) was cyclic with 15 min of treatment at 375 K and 30 min of cooling time.

The study of the phase transformation in the *MeC* blends has been done using XRD data which was collected for the test samples selected after a certain milling time with DRON-4 (CoK α radiation) automatic diffractometer. The diffraction patterns were obtained in a discrete mode: observation range $2\theta = (20\text{--}130)^\circ$, step scan of 0.05° , and counting time per step at 3 s. The peak positions and integral intensities of the reflections observed

were determined using full profile analysis. Interpretation of the X-ray diffraction data obtained have been carried out using the original software package elaborated by us using known algorithms [10] and containing full complex of standard Rietveld procedure (qualitative and quantitative phase analysis using PDF data, lattice parameters refinement; testing of the structure models and refining of all crystal structure parameters (more details are presented in Ref. [11] and at www.x-ray.univ.kiev.ua). The average crystalline size D and lattice strain ε were determined from XRD peak broadening in two ways: by the classical Williamson–Hall plots [12] and by the approximation method [11].

For elemental analysis of the final milling products an energy-dispersive X-ray spectroscopy method (EDS) has been carried out using scanning electron microscope ZEISS EVO 50XVP.

Results and discussion

A set of experiments on mechanical alloying of the equiatomic Me :CNTs (1:1) mixtures containing raw metals (**Table 1**) and CNTs has been performed to study the process of MeC carbides formation. According to XRD results of the test samples selected after each 30 min of processing, MeC monocarbides become the main constituents of the test samples processed for 250–400 min, while the samples selected at earlier milling stage contain some amount of raw metals (**Fig. 1** for TiC).

Table 1. Raw metallic materials and characterization of the MeC carbides.

Metal / Carbide		a (nm) and Me content (at. %) for MeC milling products	a (nm) and Me content (at. %) for conventional MeC carbides
Ti / TiC	Powder, <125 μ m	0.4297(9) 48.3 (XRD) 48.8 (EDS)	0.4327 51.3
Zr / ZrC	Filings, <200 μ m	0.4651(8) 49.6 (XRD) 49.2 (EDS)	0.4693 51.3
Hf / HfC	Chips, <200 μ m	0.4589(1) 50.0 (XRD)	0.4642 50.0
V / VC	Filings, <200 μ m	0.4154(5) 47.0 (XRD) 46.6 (EDS)	0.4167 53.1
Nb / NbC	Powder, < 40 μ m	0.4447(2) 46.8 (XRD) 45.3 (EDS)	0.4470 51.3
Ta / TaC	Filings, <200 μ m	0.4435(9) 46.7 (XRD) 47.7 (EDS)	0.4456 51.3

It should be noted that lattice parameters obtained at mechanical alloying are significantly lower than those for conventional monocarbides (**Table 1**). According to phase analysis results, the formation of MeC monocarbides is accompanied by wear debris. Therefore, some

test samples along with the *MeC* phase contain an admixture of the α -Fe phase, the amount of which increases with processing time increasing (Fig. 1).

Figure 1. XRD patterns of the Ti-CNT milling products. CuK α radiation.

In order to eliminate the samples from the iron contamination all powders milled were treated in a 50 % solution of hydrochloric acid and 5 times washed in distilled water away from the FeCl₂ precipitate. The purified powders were dried at room temperature for 48 hours. According to EDS data the content of iron in such powders treated in HCl does not exceed 0.2 wt. %.

All XRD patterns of milling products reveal a significant broadening of the diffraction peaks from which the average values of crystalline size *D* and lattice strain ε were estimated. So, *D* values for mechanically alloyed *MeC* are equal to 10 - 30 nm (the highest *D* value is inherent to HfC carbide and the least *D* value - to VC) (Table 2) as well as the lattice strains ε are equal to 1.5 – 2.5 %.

Figure 2. XRD patterns of the milling products after annealing at 700 °C for 2 h under argon atmosphere (IVb metals). CoK α radiation.

Figure 3. XRD patterns of the milling products after annealing at 700 °C for 2 h under argon atmosphere (Vb metals). CoK α radiation..

Unfortunately, due to a broadening of the diffraction peaks at the diffraction patterns of the final milling products it is impossible to refine the crystal structure of the carbides

formed. Consequently, the chemically treated samples have been annealed for 2 h at 700 °C under argon atmosphere in order to diminish additional microdeformations of the crystal lattice. As a result while maintaining D values ε meanings decrease to 0.5 – 1.0 % that improve the overall appearance of the X-ray patterns. Thus, chemically treated and annealed at 700 °C final milling samples contain the *MeC* monocarbides only, XRD patterns for which are presented at **Figure 2** (IVb metals) and at **Figure 3** (Vb metals).

Thus, due to the sharpening of diffraction peaks it becomes possible to make a refinement of the crystal structure of *MeC* phases. Calculations required have been made in a framework of the NaCl-type structure (*Fm3m* space group): *Me* atoms are placed in 4(*a*) 0 0 0 and C atoms are placed in 4(*b*) 0.5 0.5 0.5.

In doing so, we have refined both the occupations of 4(*a*) and 4(*b*) positions by atoms and the isotropic temperature factors. The validity of these calculations was confirmed by the reliability factor RB that did not exceed 0.04 for each phase. However, in addition to the model proposed for NaCl-type structure with 4 (*a*) and 4 (*b*) positions partially filled by metal and carbon atoms, the variant of modified NaCl-type structure is also possible, in which the partial filling of 8(*c*) 0.25 0.25 0.25 position by additional carbon atoms realizes. Calculations fulfilled have revealed that the placing of additional carbon atoms in 8(*c*) position

significantly improves the value of RB factor (up to 0.006). Finally, the results of *MeC* crystal structure refinement have revealed the existence of vacancies in 4(*a*) position filled with the metal atoms as well the existence of vacancies in 4(*b*) and especially in 8(*c*) position occupied with the carbon atoms. Presence of vacancies in a metal sublattice results in a significant shift of the *MeC* composition to the carbon side, which was also confirmed by EDS data (**Table 1**).

XRD results obtained here have revealed that the milling time required for a complete transformation of the raw components into a corresponding monocarbide correlates with the enthalpy of formation (ΔH_0^f) of the appropriate carbide (**Table 2**). Namely, if value ΔH_0^f for the *MeC* phase is lower (more negative), the process of its formation is thermodynamically more favorable. So, regardless of the type of raw metals (powders, chips or filings) the *MeC* monocarbides studied can be arranged by the simplicity of their formation in a ball mill (from less to longer processing time) as $\text{HfC} \rightarrow \text{ZrC} \rightarrow \text{TiC} \rightarrow \text{TaC} \rightarrow \text{NbC} \rightarrow \text{VC}$. To be noticed is that this correlation was also revealed in Ref. [4] for mechanical alloying of TiC, ZrC, VC and NbC monocarbides. Moreover, the enthalpy value of monocarbide formation proved to be a suitable parameter to analyze the character of a crystalline size change in these phases (**Table 2**). Obviously, there is a strong correlation between ΔH_0^f and D values: the higher the enthalpy of formation, the smaller

grain size of the corresponding *MeC* phase (Figure 4).

Table 2. Crystalline sizes for *MeC* monocarbides forming in a ball mill and enthalpy of formation for conventional carbides

Carbide	Final milling time	Crystalline size $D, (nm)$	Enthalpy of formation, ΔH_f^0 , (kJ/g·atom)
TiC	210	22(2) ¹⁾ 21(1) ²⁾	-82.52
ZrC	210	26(2) 18(1)	-97-104
HfC	210	29(3) 24(1)	-102.41
VC	410	12(2) 7(1)	-57.79
NbC	300	8(1) 8(1)	-66.78
TaC	300	14(1) 9(1)	-68.41

¹⁾ Evaluated by the Williamson-Hall analysis.

²⁾ Evaluated by the approximation method.

In our opinion, the presence of structural vacancies in the metal sublattice is responsible for a decrease of the lattice parameters of *MeC* monocarbides obtained by mechanical alloying (Table 1).

So, based on the XRD results, it follows that the milling process of the *Me*-CNTs charge takes place in several stages. At the first stage (up to 60 min of milling) the total energy of the colliding balls in a planetary ball mill is spent predominantly on the CNTs amorphization [13]

and on the raw metals fracture at the grain boundaries. The combined effect of these processes results in a penetration of the carbon atoms into the grain boundaries of metal particles at milling.

Figure 4. Crystalline size D (a) and concentration of vacancies in metal sublattice C_{vac} (b) in *MeC* monocarbides as a function of enthalpy of their formation.

At the second stage (over 60 min of milling) the amorphous carbon particles actively interact with IVb/Vb metal forming the defect lattice of *MeC/Me₂C* carbide (Nb₂C or Ta₂C). At that, the final time of this process is determined by the enthalpy of formation of appropriate carbide. Namely, if the process of formation is thermodynamically more favorable, the carbide with more perfect lattice is formed within shorter time. That is why the monocarbides studied could be arranged not only by the simplicity of their formation in a ball mill (on formation time) but also by the imperfection of their crystal lattice (degree of its

filling by the metal atoms) as $\text{HfC} \rightarrow \text{ZrC} \rightarrow \text{TiC} \rightarrow \text{TaC} \rightarrow \text{NbC} \rightarrow \text{VC}$.

In our opinion, the main advantage of the mechanical alloying method consists in a possibility of performing the synthesis of multicomponent carbides, existing of which have been predicted in terms of CASTEP (Cambridge Serial Total Energy Package) simulation program for $\text{Ti}_x\text{Zr}_{1-x}\text{C}$, $\text{Ti}_x\text{Hf}_{1-x}\text{C}$ and $\text{Hf}_x\text{Zr}_{1-x}\text{C}$ [14]. Moreover, the nanostructured (Ti,Zr)C carbide was manufactured in Ref. [15] and have revealed the hardness up to 40 GPa, which is comparable to the hardest transition metal carbides. Therefore, we are certain that mechanical alloying of the CNT containing charge gives us the possibility to create new nanoscaled superhard mixed carbides with a high potential in various engineering applications.

Conclusions

In this paper, the nanoscaled (up to 30 nm) TiC, ZrC, HfC, VC, NbC and TaC monocarbides with the modified NaCl-type structure have been synthesized from elemental metals and carbon nanotubes by mechanical alloying in a high energy planetary ball mill. It was shown that mechanical alloying is accompanied by a steady decrease in the lattice parameters of the *MeC* formed that is caused by a decrease of the total number of atoms in the *MeC* structure, i.e. by the increase of structural vacancies in the materials obtained. In this case, the partial lattice volume for the IVb group

(TiC, ZrC, HfC) of the carbides synthesized is very close to that for conventional carbides, while these values for Vb carbides (VC, NbC, TaC) are some higher. It was shown that the monocarbides obtained could be arranged by the simplicity of their formation in a ball mill as $\text{HfC} \rightarrow \text{ZrC} \rightarrow \text{TiC} \rightarrow \text{TaC} \rightarrow \text{NbC} \rightarrow \text{VC}$.

It could be supposed that substitution of graphite for carbon nanotubes in a charge is more advantageous for monocarbide manufacturing since the use of CNTs shortens the synthesis time and allows us to provide the synthesis of multicomponent carbides systematically.

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