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Mechanochemical Synthesis of Metal Carbides Using Carbon from Plant Raw Material

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Abstract

Mechanochemical synthesis of titanium and tungsten carbides involving carbon modifications obtained from the wastes of agricultural plants was developed. The conditions that affect the progress of mechanochemical synthesis of tungsten and titanium carbides were studied.

Key words: renewable plant raw materials, titanium carbide, tungsten monocarbide, mechanochemical synthesis, mechanical activation, polymethylmethacrylate, aromaticity, structure of carbon modifications, cold isostatic pressing, high temperature sintering

INTRODUCTION

It is necessary to develop resource-saving and economically admissible technologies for the synthesis of innovative ultrastrong materials [1?4]. At present, two key approaches to the development of functional materials from plant resources are known: selective extraction of chemical elements followed by obtaining the substances and materials, and integrated processing of renewable plant raw material with the maximal use of the majority of chemical elements that are present in it. Technologies based on pyrolysis and mechanochemical treatment may be a demonstrative example [4–12].

The subject of special interest in modern materials science and powder metallurgy is refractory compounds, in particular carbides of tungsten and titanium; these compounds possess a complex of physicochemical, mechanical and technological properties. Due to this fact, they may win broad application for manufacturing constructional and instrumental ceramics, nanocomposite systems, anticorrosive and wear-resistant coatings.

An urgent problem for the formation of tungsten and titanium carbides is the search for efficient carbon modifications with a specific set of properties on which the chemical composition of the refractory compound to be synthesized depends, with the possibility to vary its stoichiometric composition and a decrease in the duration of mechanochemical synthesis, therefore, a decrease in energy consumption [6, 7, 13].

Among efficient modifications of carbon, it is necessary to mention the products of pyrolysis prepared from renewable plant material – the wastes of agricultural crops. In comparison with carbon modifications obtained from hydrocarbon raw material, these products have specific chemical composition, a good set of physicochemical, mechanical and technological properties [5, 6, 13]; in addition, they are ecologically friendly.

In the mechanochemical technology of obtaining tungsten and titanium carbides, amorphous modifications of carbon are used as the carbon-containing component: carbon black of PM-15 grade, activated carbon for medical purposes. It was noted that the synthesis of titani-

um carbide according to the explosion-involving kinetics is not realized if graphite is used as the carbon-containing component at any concentration in the reaction mixture [7, 8, 13].

The goal of the present work was to study the technology of mechanochemical synthesis of tungsten and titanium carbides using carbon modifications obtained from renewable plant raw material – wastes of agricultural crops.

EXPERIMENTAL

Preparation of carbon modifications

Carbon modifications with amorphous, amorphous-crystalline and crystalline structures as the major component for the synthesis of tungsten and titanium carbides were obtained with the help of pyrolysis at a temperature of (°C): 900, 1150, 1300, 1500. Initial materials were various kinds of renewable plant raw materials (crop wastes): oats husks (Allyur variety), wheat (Dobrynya variety), and buckwheat husks (Agidel variety) [9–13].

Synthesis of tungsten carbide

High temperature mechanochemical synthesis of tungsten carbide was carried out in a specially developed vibration set-up [13, 14] providing high energy strain due to the large amplitude of vibrations of the mechanical reactor (A = 90 mm).

The synthesis of powdered tungsten carbide WC was carried out using tungsten oxide WO_3 of "kh. ch." reagent grade. Reducing metal was Mg (99.95 %), while carbon-containing component was carbon modification from oats husk (Allyur variety) obtained at a temperature of 900 °C and close in structure to carbon black of PM-15 grade, a classical carbon agent for the synthesis of tungsten carbide. Polymethylmetacrylate (PMMA) in the amount of 1–3 % of the mass of initial components was added into the mixture as additional ingredient. Polymethylmetacrylate was chosen because of its ability to undergo mechanical destruction readily and to form a substantial amount of carbon compounds during mechanical activation. The mass of initial components was 30 g.

The milling bodies in the vibratory mill were the balls made of ShKh15 grade steel 12–14 mm in diameter. The reactor was filled with balls by not more than 40 % of its volume because for larger fraction of filling the efficiency of vibratory mill decreases. The progress of synthesis was followed by observing a jumpwise temperature rise in the reactor; temperature was measured with the help of the infrared laser pyrometer S-20.1 with the error of 0.1 °C.

The kinetics of tungsten carbide synthesis was studied using the thermograms plotting the temperature in the mechanical reactor *vs*. time of mechanical activation. The synthesis in progress was controlled relying on the changes of the temperature at the external wall of the mechanical reactor. At the moment of the start of synthesis, due to the exothermal effect, a sharp increase in temperature was observed; after the maximal temperature was achieved, milling was stopped. Then the mechanical reactor was removed from the mill, cooled, the reaction product was taken out of the reactor and washed in boiling 20 % HCl solution for 30 min. To remove admixtures, the powders were subjected to double washing with distilled water; residual moisture was removed with acetone.

Synthesis of titanium carbide

Titanium powder of PTES-2 grade with particle size 150–200 μm and 99.8 % purity was used. As carbon-containing materials, we used the husks of oats (Allyur variety), wheat (Dobrynya variety), buckwheat (Agidel variety). The plant raw materials were sieved preliminarily to remove foreign inclusions, washed in distilled water, then dried at a temperature of 100–110 °C and ground in a DESI-11 disintegrator (Estonia) to the particle size of ~300 μm. Carbon modifications with amorphous, amorphous-crystalline and crystalline structures were obtained with the help of pyrolysis at the same temperatures as in the case of WC synthesis (900, 1150, 1300 and 1500 °C). Calculation of the components was carried out relying on the stoichiometry of titanium carbide to be synthesized $TiC_{0.8}$. Mechanochemical synthesis was carried out in a vario-planetary mill Pulverisette-4 (Fritsch, Germany). Milling bodies were the balls made of the hard alloy VK-6 15 mm

in diameter. The mechanical reactor of the mill as a tight container made of corrosion-proof mill with an insert of the hard alloy VK-6 with the inner diameter 75 mm and the height of 70 mm. The following mode was used fort he synthesis of titanium carbide in the vario-planetary mill: the frequency of rotation of the main disk 400 rpm, of satellites – 800 rpm; the atmosphere was the air; the intensity (the ratio of the mass of initial materials to the mass of milling balls) 1 : 27; the degree of mechano-reactor filling 30 %. Depending on the type of the used carbon-containing raw material, the duration of the delay of mechanochemical synthesis (the time from the start of mechanochemical activation to the moment of the jumpwise temperature rise) was 22.5 to 135 min. Temperature and pressure in the mechanical reactor during the mechanochemical synthesis were controlled with the help of a radio-controlled cap of the GTM system incorporated in the vario-planetary mill.

Compaction and high temperature sintering of the samples of tungsten and titanium carbides

Compaction of the samples of synthesized tungsten and titanium carbides was carried out with the help of cold isostatic pressing using the laboratory isostatic press if LCIP42260 model (Avure Technologies Inc., the USA).

Sintering of experimental samples of tungsten and titanium carbides was carried out in a high-temperature furnace (Nabertherm, Germany) of RHTH 120-300/18 series in the atmosphere of nitrogen.

The phase composition of the synthesized carbon modifications and titanium carbide was determined by means of X-ray phase analysis using a D8 ADVANCE diffractometer (Germany) in CuK_α radiation according to the standard procedure. Identification of the compounds incorporated into the samples under study was carried out in the automatic search mode EVA using the powder database PDF-2.

Particle side distribution and granulometric composition were established with the help of an Analysette 22 NanoTec/MicroTec/XT laser particle analyser (Fritsch, Germany).

The morphology of carbon-containing raw material was studied with the help of the inversed metallographic microscope MT 8530 (Meiji Techno, Japan) equipped with the Thixomed PRO programme (Russia).

Sulphur and carbon content in carbon modifications and titanium carbide powders was determined with the help of sulphur and carbon analyser CS 600 (LECO, the USA).

The fragment composition of carbon modifications was studied using a NMR spectrometer Mercury-plus 300 (Varian, the USA). The resolution was 0.5 Hz with the ampoules 5 mm in diameter.

Isolation and sampling of the synthesized compounds were carried out after cooling of the mechanical reactor to room temperature in the box of the third class biological safety AC_3 (Esco, Singapore) equipped with vacuum drying and ultrasonic bath.

RESULTS AND DISCUSSION

Temperature of the external wall of mechanical reactor at the moment of mechanochemical synthesis of tungsten carbide increases with an increase in the mass of PMMA loaded into the reactor (Table 1). The duration of mechanical activation of the mixture of initial components necessary for reaction initia-

TABLE 1

Parameters of mechanochemical synthesis of tungsten carbide

PMMA content in the mixture WO_3 + Mg + C, %	Time of mechanical activation of initial mixture, s	Temperature of the external wall of mechano-reactor, °C
0	260	135
1	332	141
2	353	147
3	431	159

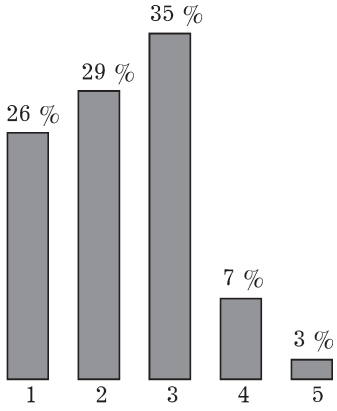

Fig. 1. Size distribution of tungsten carbide particles (μm): 0.2–0.5 (1), 0.5–2 (2), 2–5 (3), 5–8 (4), 8–10 (5).

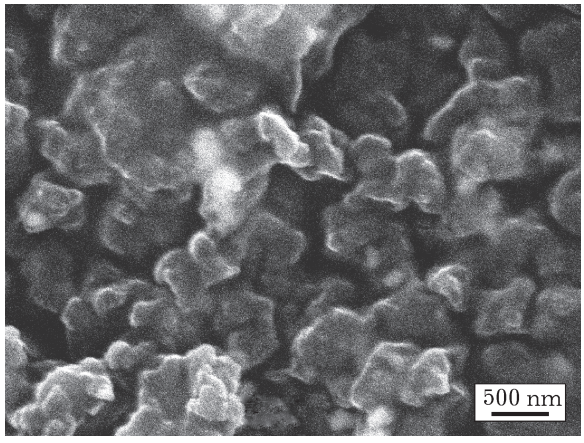

Fig. 2. Tungsten carbide particles decorated with deposited gold.

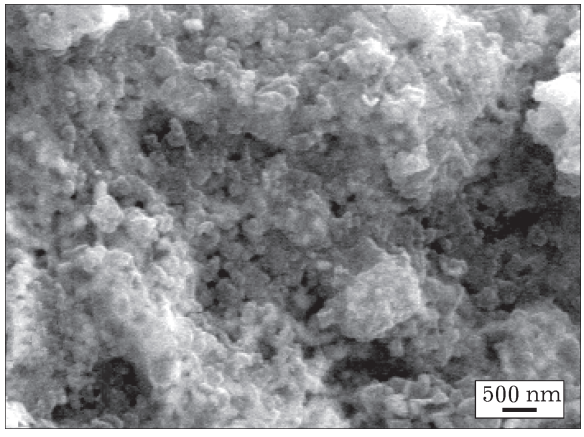

Fig. 3. Surface of tungsten carbide particle formed by consolidation of the particles 200–300 nm in size.

tion, that is, the time delay of mechanochemical synthesis also increases,

After the introduction of PMMA, the time necessary for the initiation of mechanochemical reaction and thermal effect increase. However, an increase in PMMA content in the initial components mixture above 3 % is unreasonable because after mechanochemical synthesis and depressurization of the mechanical reactor we observe the presence of excess carbon on the inner walls of the reactor and in reaction products. This excess carbon did not participate in the synthesis of tungsten carbide. With an increase in PMMA content in the mixture charged into the reactor, the time of delay of the mechanochemical synthesis increases substantially. This is connected with damping of mechanical energy supplied to the initial components of the mixture, caused by polymethylmetacrylate and the products of its mechanical destruction.

With an increase in the amount of PMMA added to the mixture of initial components for the mechanochemical synthesis of tungsten carbide, a decrease in W_2C phase content is observed. The X-ray analysis of powders obtained after washing showed that after the addition of 3 % PMMA into the initial mixture the product consists of tungsten monocarbide WC. The presence of W_2C and residual magnesium oxide was not revealed. As PMMA content increased in the mixture of initial components, the amount of recorded carbon that did not participate in the mechanochemical reac-

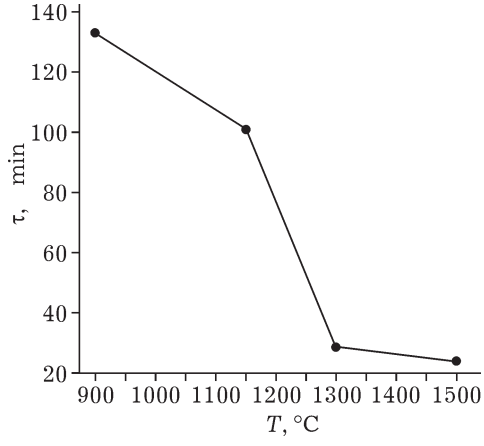

Fig. 4. Effect of the temperature of plant material (oats husks) pyrolysis on the time of delay of mechanochemical synthesis (τ).

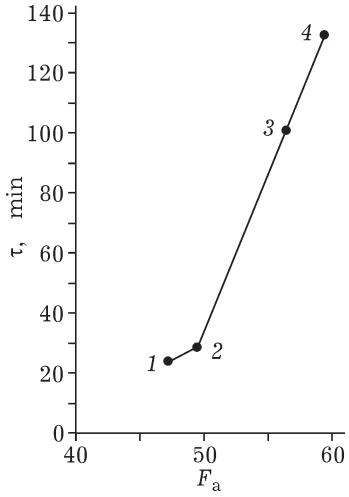

Fig. 5. Effect of the degree of aromaticity (F_a) on the time of delay of mechanochemical synthesis of titanium carbide. Temperature of pyrolysis of carbon obtained from oats husks (°C): 1500 (*1*), 1300 (*2*), 1150 (*3*), 900 (*4*).

tion decreased. Measurements of the fractional composition of tungsten carbide powder showed that it is composed of the particles 20 nm to 10 μm in size (Figs. 1–3).

So, mechanochemical treatment of the mixture of initial components containing PMMA allows us to synthesize tungsten carbide powder without admixture of W_2C phase.

Carbon modifications obtained as a result of pyrolysis of plant raw material were used as carbon-containing component for the mechanochemical synthesis of titanium carbide. Specific surface area (one-point BET method) of carbon modifications synthesized from plant raw material was 140 to 220 m^2/g. To reveal comparative characteristics, we also used carbon black of PM-15 grade which is recommended as an optimal carbon-containing agent [5].

It was established that the structure (amorphous, amorphous-crystalline, crystalline) of carbon modifications obtained at different pyrolysis temperatures affects the duration of the delay of mechanochemical synthesis (Fig. 4).

To reveal the limiting factors affecting mechanochemical synthesis of titanium carbide, we carried out a NMR investigation of the fragmentary composition of carbon modifications obtained at different pyrolysis temperatures. It was established that the origin of carbon modifications most strongly affects the degree of

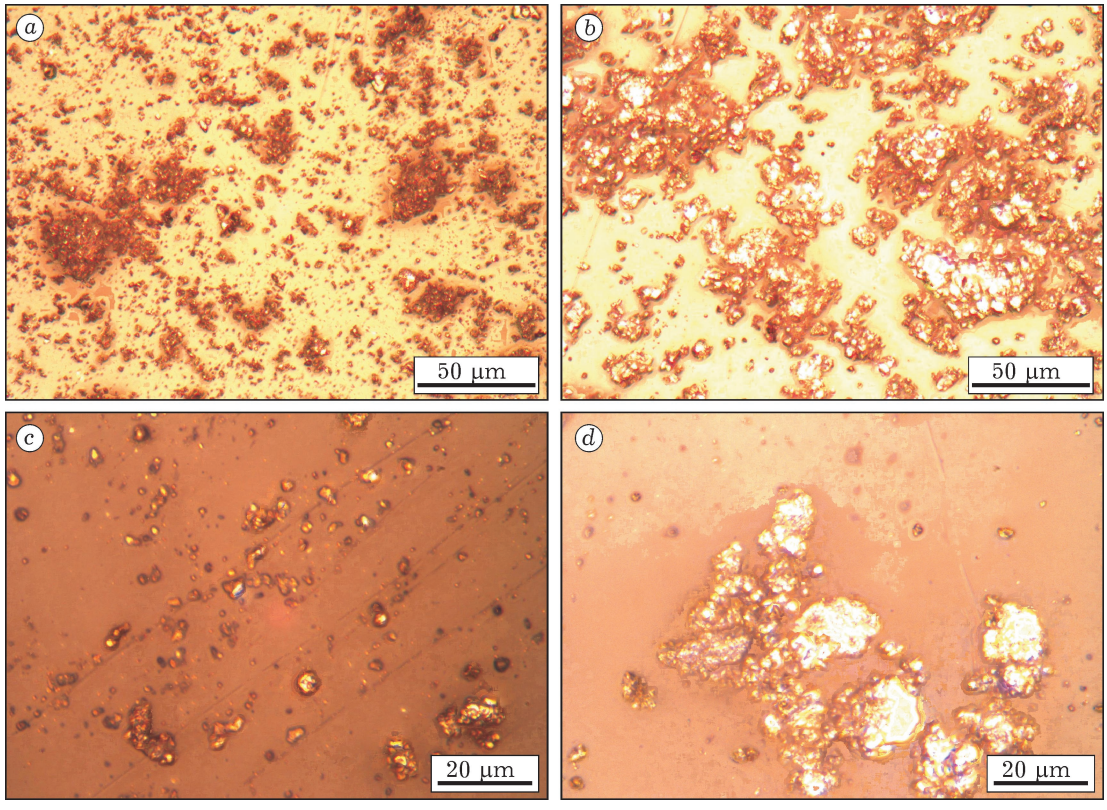

Fig. 6. Morphology of titanium carbide particles. Pyrolysis temperature (°C): 900 (*a*), 1150 (*b*), 1300 (*c*), 1500 (*d*) (×500 (*a*, *b*), ×1000 (*c*, *d*)).

TABLE 2

Sulphur content in carbon modifications obtained from plant raw material, %

Carbon black PM-15	*T*, °C	Carbon modification		
		from oats husks	from wheat husks	from buckwheat husks
0.65	1300	0.04	0.075	0.14
	1500	0.024	n/d	n/d

Notes. 1. Here and in Table 3: *T* is temperature of plant material pyrolysis. 2. n/d – not determined.

TABLE 3

Content of free carbon (C_{fr}) and sulphur in titanium carbide synthesized using carbon modifications obtained from different materials

Materials	*T*, °C	Content, %	
		C_{fr}	S
Oats husks	1500	0.23	0.009
« «	1300	0.35	0.012
Wheat husks	1300	0.47	0.075
Buckwheat husks	1300	0.58	0.085
PM-15 carbon black	–	0.50	0.19

Note. For designations, see Table 2.

aromaticity, which changes from 59.4 (for carbon modification from oats husks) to 85.1 (for carbon modification from buckwheat husks).

The effect of the degree of aromaticity on the delay of mechanochemical synthesis of titanium carbide depending on pyrolysis temperature of carbon obtained from oats husks is presented in Fig. 5.

One can see that an increase in the temperature of plant material pyrolysis causes a decrease in the degree of aromaticity and shortening of the time of delay of mechanochemical synthesis of titanium carbide. So, the minimal degree of aromaticity is characteristic of carbon modification with crystal structure, while the maximal one is characteristic of carbon modification with amorphous structure.

The morphology of titanium carbide powder synthesized using carbon modification from oats husks at different pyrolysis temperatures is presented in Fig. 6.

The highest dispersity is characteristic of the powder synthesized using carbon with graphitised structure, which was obtained by pyrolysis of organic raw material at a temperature of 1300 °C (see Fig. 6, *c*). An increase in pyrolysis temperature to 1500 °C causes partial agglomeration and an increase in particle size of the synthesized powder (see Fig. 6, *d*).

Analysis of powders, carried out with a laser analyser, showed that the size of titanium carbide particles is 0.5–40 μm, and 80 % of the particles have the size less than 10 μm.

The effect of pyrolysis mode on sulphur content in carbon modifications is shown in Table 2. One can see that sulphur content in PM-15 carbon black obtained from hydrocarbon raw material exceeds it content in carbon modifications from plant raw material by a factor of 4 to 25. The best results are observed for carbon modification synthesized at a temperature of 1500 °C from oats husks.

The effect of pre-history of carbon modifications on sulphur and free carbon (C_{fr}) content in titanium carbide is presented (Table 3).

Sulphur content in titanium carbide synthesized with the use of carbon modifications obtained by the pyrolysis of the plant raw material is 2–20 times lower than that in titanium carbide synthesized using carbon black PM-15.

CONCLUSIONS

1. The conditions affecting the mechanochemical synthesis of tungsten and titanium carbides were studied.

2. The final product in which the W_2C phase is absent was obtained by means of explosion mechanochemical synthesis through the vibrational treatment of initial mixture containing polymethylmetacrylate.

3. It is established that important role in the mechanochemical synthesis of titanium carbide involving carbon obtained from plant material is played by the structure of carbon modifications and the degree of their aromaticity. The synthesis proceeds more easily with crystalline carbon than with amorphous one.

4. Tungsten and titanium carbides synthesized using carbon modifications from plant raw material possess acceptable chemical composition for the development of functional coatings and solid alloys.

5. Compact samples of tungsten and titanium carbides were obtained by means of cold isostatic pressing followed by high temperature sintering.

REFERENCES

1 Zhukov M. F., Cherskiy I. N., Cherepanov A. N., Kovalenko N. A., Saburov V. P., Galevskiy G. V., Andrianova O. A., Krushenko G. G.,Uprochneniye Metallicheskikh, Polimernykhi Elastomernykh Materialov Ultradispersnymi Poroshkami Plazmokhimicheskogo Sinteza, Nauka, Novosibirsk, 1999, p. 312.

2 Popovich A. A., Reva V. P., Vasilenko V. N., *Porosh. Metallurgiya*, 11 (1992) 22.

3 Onishchenko D. V., Reva V. P., *Fiz. Khim. Obrab. Mater.*, 2 (2011) 71.

4 Kiparisov S. S., Levinskiy Yu. V., Petrov A. P., Karbid Titana: Polucheniye, Svoystva, Primeneniye, Metallurgiya, Moscow, 1987, p. 216.

5 Onishchenko D. V., Tsvetnikov A. K., Popovich A. A., Kuryavy V. G., *Zh. Prikl. Khim.*, 81, 5 (2008) 1050.

6 Onishchenko D. V., Chakov V. V., *Zh. Prikl. Khim.*, 84, 9 (2011) 1562.

7 Popovich A. A., Mekhanokhimicheskiy Sintez Tugoplavkikh Soyedineniy, Izd-vo DVGTU, Vladivostok, 2003, p. 201.

8 Popovich A. A., Vasilenko V. N., Abbakumov E. G., Osobennosti Makhanokhimicheskogo Sinteza Karbida Titana (Treatises), Nauka, Novosisbirsk, 1991, pp.176–183.

9 RU Pat. No. 67777, 2007.

10 RU Pat. No. 72358, 2008.

11 RU Pat. No. 2327255, 2008.

12 RU Pat. No. 2340042, 2008.

13 Onishchenko D. V., Popovich A. A., Wang Qingsheng, *Izv. Vuzov. Porosh. Metallurgiya Funkts. Pokrytiya*, 2 (2011) 9.

14 Onishchenko D. V., Reva V. P., *Fiz. Khim. Obrab. Mater.*, 2 (2011) 71.