

# Carbide-nanopowders produced by electrical explosion of wires

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Phase compositions of nanopowders prepared by electrical explosion of tungsten, titanium and aluminium wires in liquid hydrocarbons ( $C_6H_6$ ,  $C_6H_{14}$ ,  $C_6H_5CH_3$ , and  $C_{10}H_{22}$ ), multicomponent reactionary surroundings such as hexamethylenetetramine-decane suspension, and solid paraffin were investigated. It has been established that the output of carbon-saturated carbide phases increases with increasing density and dynamic viscosity of the working medium as well as consumed energy, and depends on elemental composition of hydrocarbons (C/H ratio in hydrocarbon molecules). The content of the carbide phases depends on the values of the upper warm-up border of chemical compounds stability.

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## 1. Introduction

Refractory compounds including metal carbides are widely used in science and engineering to produce cutting tools and parts of machines and mechanisms operating at high temperatures and to modify cast alloys. The characteristics of various functional materials can be improved with the use of nanopowders (NP). One of the methods to produce nanodispersed metal carbide powders is electric explosion of wires (EEW) in carbon-containing media.

The electric explosion of wires is the process of explosive destruction of a metal wire under the action of great density current ( $>10^{10}$  A/m<sup>2</sup>) [1]. This process accompanies by the scattering products, shock waves and electromagnetic radiation. Material of the wire transmutes into particles of nanosized range (10...100 nm) in accordance with certain conditions. The formation of particles in EEW process occurs in the presence of strongly nonequilibrium conditions – the large gradients of temperature and speeds of cooling ( $> 10^7$  K/s), intensive heat transfer and mass transfer, ionization, mixture, influence of electric and magnetic fields. EEW in inert gases or hydrogen is used to produce powders of metals, alloys, and intermetallic compounds. EEW in chemically active gases is used to produce nanopowders of chemical compounds of metals: oxides, nitrides, carbides, etc.

The applicability of the EEW method for synthesis of metal carbides such as  $Al_4C_3$ ,  $LaC_2$ , TiC, ZrC, NbC,  $Nb_2C$ ,  $Ta_2C$ , MoC, and  $W_2C$  by explosions in ethane, isobutene, acetylene, and mixture of acetylene-argon was demonstrated in [2, 3]. Tungsten, tantalum, and titanium carbides were prepared in [4] in acetylene-argon and propane-argon media by the EEW method. EEW in gas media results in obtaining carbides deficient in carbon ( $W_2C$ ,  $WC_{1-x}$ , and  $Ta_2C$ ).

The density of reactants is much higher during wire explosions in condensed media compared to explosions in gases. That fact allows the chemical compounds output to be increased and their phase composition to be changed.

This paper reports the study of the influence of the EEW energy parameters, density and dynamic viscosity of the surrounding ambiances, elemental composition of hydrocarbons (C/H ratio in hydrocarbon molecules) on the phase compositions of nanopowders prepared by electrical explosion of tungsten, titanium and aluminium wires in liquid hydrocarbons ( $C_6H_6$ ,  $C_6H_{14}$ ,  $C_6H_5CH_3$ , and  $C_{10}H_{22}$ ), hexamethylenetetramine-decane suspension, and solid hydrocarbon paraffin.

## 2. Experimental details

The principal scheme of installation for producing electroexplosive powders consists of a current pulse generator, a commutator, and a discharge chamber [5]. Hexane  $C_6H_{14}$ , decane  $C_{10}H_{22}$ , benzene  $C_6H_6$ , toluene  $C_6H_5CH_3$ , and suspension hexamethylenetetramine  $(CH_2)_6N_4$  in decane were used as working surrounding ambiances for EEW. Hydrocarbons were taken as reagents because they can give active atoms of carbon during thermodestruction, and hexamethylenetetramine can give active atoms of nitrogen. Volume of liquid in the discharge chamber was a liter. Concentration of hexamethylenetetramine was 50 g/l. The powder of hexamethylenetetramine was suspended in decane and ultrasonically treated for 15 min before experiment to increase the stability to sedimentation.

The tungsten, titanium and aluminium wires with diameter  $d = 0.2...0.3$  mm and length  $l = 50...120$  mm were used in experiments. The wires were exploded in the fast-explosion mode with infinite current pause when almost all accumulated in capacitor energy was consumed by wire. The specific electrical energy input in the wire ( $e$ )

was changed from 0.4 to  $1.5e_s$ ;  $e_s$  is the sublimation energy of the wire material. Parameters of electric circuit: capacitance  $C = 1.2 \mu\text{F}$ ; charging voltage  $U = 15 \dots 30 \text{ kV}$ ; inductivity  $L = 0.9 \mu\text{H}$ .

The semiquantitative phase analysis of the powder composition was performed using  $\text{CuK}\alpha$ -radiation of a DRON-3.0 X-ray diffractometer. Particle shapes and the dispersity were determined by means of a JSM-840 scanning electron microscope. The determination of specific surface area ( $S_{\text{sp}}$ ) carried out by using a method of low temperature nitrogen adsorption (BET). The differential-thermal analysis (DTA) and thermogravimetric analysis (TGA) was performed with apparatus Q-1000.

### 3. Results and discussion

According to the X-ray data, powders prepared by EEW in liquid hydrocarbons contain the carbides phases and residual metal (Table 1).

Table 1. Phase Composition of Powders prepared by Electrical Explosion of Tungsten, Titanium and Aluminium Wires

Material of the wire being exploded	Surrounding ambience of the EEW	Phase composition of the EEW products
W	Hexane	W, $\text{W}_2\text{C}$ , $\text{WC}_{1-x}$
W	Decane	$\text{WC}_{1-x}$ , $\text{W}_2\text{C}$ , W
W	Benzene	$\text{WC}_{1-x}$ , $\text{W}_2\text{C}$ , W
W	Toluene	$\text{WC}_{1-x}$ , $\text{W}_2\text{C}$ , W
W	Paraffin	WC, W
Ti	Decane	TiC, Ti
Al	Decane	Al, $\text{Al}_4\text{C}_3$

The WC compound exists in several phases, including the low-temperature phase  $\alpha$ -WC, the high-temperature phase  $\beta$ -WC, and a number of phases  $\text{W}_2\text{C}$  that differ in their lattice parameters [6]. The  $\text{W}_2\text{C}$  phase has the hexagonal close-packed lattice and several other crystalline phases ( $\gamma$ -,  $\varepsilon$ -,  $\beta$ -, and  $\alpha$ -phases) that differ in the degree of ordering of the carbon atoms in the octahedral vacancies of the closest packing of tungsten atoms. The low-temperature phase of tungsten monocarbide ( $\alpha$ -WC) has a simple hexagonal structure. The high-temperature phase of  $\beta$ -WC crystallizes into the face-centered cubic (FCC) lattice that is stable at temperatures exceeding 2800 K.  $\beta$ -WC phase can be considered as nonstoichiometric FCC carbide  $\text{WC}_{1-x}$ , where  $0 \leq x \leq 0.41$ . According to the literature [7], nonstoichiometric carbide undergoes an ordering process upon cooling from the synthesis temperature to room temperature. The order-disorder transformations in carbides are first-order phase transformations [7] accompanied by discontinuous changes in the sample volume. At the same time, ordering is diffusion process.

Therefore, the transformation is not instantaneous, but lasts for tens of minutes. High temperatures during tungsten carbide synthesis by electroexplosion and fast cooling of the prepared powders lead to stabilization of the metastable disordered state of carbide ( $\text{WC}_{1-x}$ ).

Fig. 1 shows the qualitative composition of tungsten EEW products for the indicated liquid hydrocarbon types and a deposited energy of  $\sim 1.2e_s$ . It can be seen from the figure 1 that the tungsten carbide  $\text{WC}_{1-x}$  output increases upon increasing the C/H ratio and the liquid hydrocarbon density, whereas the metal tungsten content in the products decreases.

The influence of the consumed energy on the phase and elemental composition of EEW products was studied using decane as a working medium. According to the X-ray data, the main product of the tungsten EEW in decane was carbide  $\text{WC}_{1-x}$ . Fig. 2 shows the relative contents of W and  $\text{W}_2\text{C}$  phases, determined as ratios of the intensities ( $I$ ) of 100% reflections of these phases to the intensity of the 100% reflection of the  $\text{WC}_{1-x}$  phase.

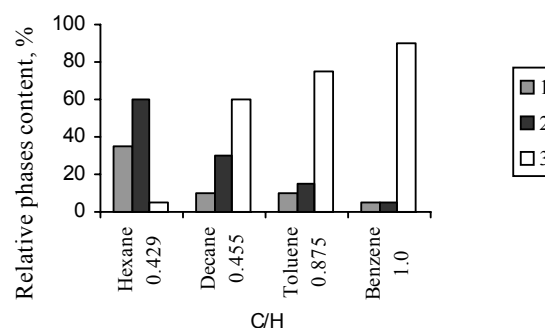


Fig. 1. Relative contents of W (1),  $\text{W}_2\text{C}$  (2), and  $\text{WC}_{1-x}$  phases (3) in tungsten EEW products having different C/H ratios.

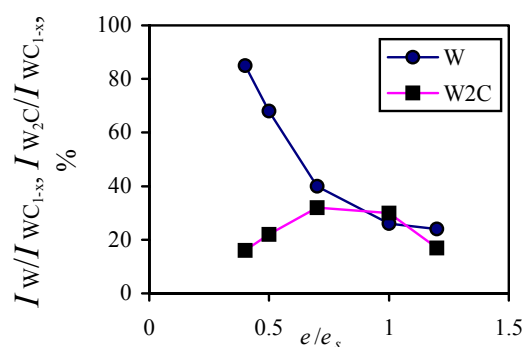


Fig. 2. Dependence of the relative contents of W and  $\text{W}_2\text{C}$  phases in the products of tungsten EEW in decane on the amount of consumed energy.

Even for the maximum consumed energy ( $e/e_s = 1.2$ ), tungsten carbide remains the nonstoichiometric compound  $\text{WC}_{1-x}$  deficient in carbon. According to the X-ray data (Table 1), EEW of tungsten in saturated solid hydrocarbon

– paraffin – allows stoichiometric carbon-saturated tungsten carbide WC to be prepared.

Scanning electron micrographs reveal that the products of tungsten EEW in decane are powders consisting of spherical particles having smooth surfaces and diameters ranging from 0.1 to 5  $\mu\text{m}$  (Fig. 3). Powder particles sizes commonly tend to decrease upon increasing the amount of consumed energy in any medium (gas, liquid, or solid).

To study the conditions for forming carbides by EEW, we compared the products of tungsten and aluminium wire electroexplosions. Aluminium carbide and unreacted aluminium (Table 1) were detected in the products of aluminium EEW in decane. Moreover, the main product was metal aluminium even at sufficiently high level of consumed energy ( $e/e_s = 1.5$ ). The relative content of aluminium carbide did not exceed 40%. The powders consisted of spherical particles having diameters ranging from 0.1 to 10  $\mu\text{m}$  and loose surfaces (Fig. 3).

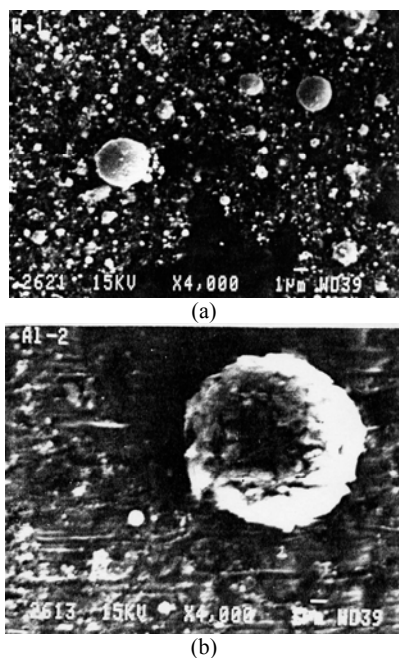


Fig. 3. SEM micrographs of powders prepared by EEW in decane for aluminium (a) and tungsten (b) wires,  $e/e_s = 1.1$ .

The analysis of the results of carbide synthesis demonstrated that the output of aluminium carbide  $\text{Al}_4\text{C}_3$  was much less than that of tungsten carbide for the same amounts of consumed energy. This low output of aluminium carbide prepared by EEW can be explained by the temperature dependence of the isobaric-isothermal potential  $\Delta G$  of the formation reaction of aluminium carbide [8]. The temperature at which aluminium carbide remains stable is limited to temperatures lower than 3000 K. During aluminium EEW in decane, the chemical reaction takes place due to diffusion of carbon atoms into the aluminium particle at temperatures below the boiling

point of aluminium metal (2720 K) is:  $4\text{Al}_{(\text{liquid})} + 3\text{C}_{(\text{gas})} = \text{Al}_4\text{C}_{3(\text{solid})}$ . In the course of this reaction, a continuous carbide layer is formed on the metal particle surface, thereby limiting the diffusion of carbon atoms into the metal. This phenomenon is also confirmed by the micrographs in which spherical particles appear to have loose surfaces.

The maximum temperature at which tungsten carbides remain stable is much higher than that for the aluminium ones. A decrease in  $\Delta G$  is observed at  $\sim 3000$  K. The particle morphology demonstrates the feasibility of forming tungsten carbides in the liquid phase (Figure 3), because the spherical particles have smooth surfaces. Hence, it follows that tungsten carbides are formed at temperatures exceeding their melting point (for example,  $T_{\text{melt}} \sim 3130$  K for  $\text{W}_2\text{C}$ ) through the diffusion of carbon atoms into the liquid tungsten particle:  $2\text{W}_{(\text{liquid})} + \text{C}_{(\text{gas})} = \text{W}_2\text{C}_{(\text{liquid})}$ . The fact that the main product of tungsten EEW in liquid hydrocarbons is nonstoichiometric tungsten carbide ( $\text{WC}_{1-x}$ ) can be explained by the high concentration of active carbon atoms in the chemical reaction and by fast cooling of the prepared powders. It is well known that  $\text{WC}_{1-x}$  remains stable at temperatures exceeding 2800 K [8]. Thus, the higher output of tungsten carbide nanopowders is a consequence of their higher thermal stability relative to those of aluminium carbides.

The activity of the prepared tungsten carbide nanopowders was estimated by differential thermal analysis from the temperature at which the oxidation began ( $T_s$ ,  $^{\circ}\text{C}$ ), the maximum oxidation rate ( $v_{\text{ox}}$ , mg/min), the degree of transformation (oxidation level) of the powders for temperatures  $\leq 1000^{\circ}\text{C}$  ( $\alpha$ , %), and the specific heat release ( $S/\Delta m$ , %). The latter is defined as the ratio of the area under the maximum of  $S$  in the heat release curve to the mass increment  $\Delta m$  of the sample ( $S/\Delta m$ , %). These parameters are presented in Table 3.

Table 2. Thermal Stability of Powders Prepared by Tungsten EEW in Decane.

$e/e_s$	$T_s$ , $^{\circ}\text{C}$	$\alpha$ , % $\leq 1000^{\circ}\text{C}$	$v_{\text{ox}}$ , mg/min	$S/\Delta m$ , %
0.4	480	10.8	2.0	100 *
0.5	560	15.4	6.3	86
0.7	570	18.8	9.0	82
1.1	540	16.5	7.0	96

Note: \* The heat effect of the sample is taken as 100%.

In the examined range of consumed energy values, the oxidation level (the mass increment of the sample on heating to  $1000^{\circ}\text{C}$ ) increased as  $e/e_s$  increased from 0.4 to 0.7 and then it decreased more slowly. Upon increasing the consumed energy and the degree of EEW product dispersion, the starting temperature for intense oxidation increased from  $480^{\circ}\text{C}$  to  $570^{\circ}\text{C}$ . Further increases in  $e/e_s$ , resulted in a decrease the temperature at which the oxidation began (to  $540^{\circ}\text{C}$ ). The dependence of the oxidation rate of EEW products on  $e/e_s$  was similar to the

corresponding dependences of the sample oxidation level and the onset temperature of intense oxidation. The heat effect of the oxidation products was most pronounced for  $e/e_s = 0.4$ , and it was least pronounced at  $e/e_s = 0.5 \dots 0.7$ .

The parameters of the thermal stability of the samples prepared by tungsten EEW in decane correlated with the dependences that the phase and elemental compositions of powders had on the consumed energy. The residual tungsten content decreased upon increasing consumed energy, whereas the output of carbides  $W_2C$  and  $WC_{1-x}$  increased.

According to the X-ray data, the products of the aluminium EEW in hexamethylenetetramine - decane suspension contained aluminium carbide, nitride and unreacted aluminium (Table 3). The products of the titanium EEW contained titanium carbide TiC and unreacted titanium.

Table 3. Phase Composition of EEW Products in Hexamethylenetetramine-Decane Suspension.

Metal	Phase composition of the EEW products	Ratio of the intensities ( $I$ ) of 100% reflections
Al	Al, $Al_4C_3$ , AlN	$I_{AlN}/I_{Al} = 22,5\%$ $I_{Al_4C_3}/I_{Al} = 25\%$
Ti	Ti, TiC	$I_{TiC}/I_{Ti} = 95\%$

The analysis of the temperature dependence of the isobaric-isothermal potential  $\Delta G$  of the reaction of titanium carbide formation [7] showed, that at temperature more than 1847 K the reaction of carbide formation is thermodynamically more probable in comparison with the reaction of nitride formation:  $Ti_{liq} + C_{sol} = TiC_{sol}$ . At temperature below 1847 K the reaction of nitride formation becomes more probable, but the formed carbide layer makes difficult the diffusion of nitrogen into the particles. That is why only titanium carbide was revealed in the products of the titanium EEW in the hexamethylenetetramine-decane suspension.

The upper warm-up borders of the thermal stability of aluminium carbide and aluminium nitride are similar. The aluminium nitride sublimates at the temperature 2723 K [8]. At  $T = 2700$  K the isobaric-isothermal potential of the forming aluminium carbide and aluminium nitride are approximately alike. In case of the aluminium EEW in the hexamethylenetetramine-decane suspension the following reactions occur:  $Al_{liq} + \frac{1}{2} N_{2g} = AlN_{sol}$ ,  $4Al_{liq} + 3C_{sol} = Al_4C_{3sol}$ . According to the X-ray data, the products of the aluminium EEW in the hexamethylenetetramine-decane suspension are the powder, containing the phases of aluminium carbide and aluminium nitride. The content of the aluminium nitride was about 20%. This circumstance is connected, obviously, with its lower thermal stability.

#### 4. Conclusions

The comparison between the formation of aluminium, tungsten, titanium carbides, and aluminium and titanium nitrides by EEW showed that the output of the chemical compounds depends on their thermal stability, i.e. the more thermally stable they are, the higher their output. Furthermore, the output of carbon-saturated carbides phases increases, whereas the residual metal content in electroexplosive products decreases, upon increasing the C/H ratio in the liquid hydrocarbons molecules and the value of the consumed energy. The content of carbide phase enriched carbon also increases upon increasing the dynamic viscosity and density of the surrounding ambience.

It is possible to obtain the nanopowders of the complex phase and chemical composition under the EEW in condensed multicomponent reactionary surroundings in condition of the similar values of the upper warm-up border of chemical compounds stability. In case of difference of these values, the compound, which is stable to higher temperature is preferentially formed.

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