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Self-Propagating High-Temperature Synthesis of Ultrafine Tungsten Carbide Powders

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1. Introduction

Transition metal carbides, particularly tungsten carbide, are rather attractive due to their physical and mechanical properties [1]. They are characterized by the high melting point, unusual hardness, low friction coefficient, chemical inertness, oxidation resistance, and excellent electric conductivity. Nowadays, highly dispersed tungsten carbide powders appear to be very important for production of wear-resistant parts, cutters, non-iron alloys, etc.

It is well known, that fine-grained alloys demonstrate better mechanical properties in comparison with coarser alloys of the same composition under the same terms [2-4]. Use of ultrafine or nanosized powders is one of the most efficient ways to produce new materials with required properties.

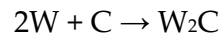
That is why nowadays the production technologies of nanopowders play the leading role among the widely used directions.

There are several phases of tungsten carbide; the most important ones are WC and W₂C [5]. Though W₂C is unstable at T=1300°C, in most cases the mixture of WC and W₂C is observed in the synthesis products. Precipitation of the single phase of WC is only possible in the narrow area of the technological parameters [6].

There are different ways to obtain tungsten carbide powders, and each process changes the characteristics of the forming product.

Tungsten carbide powders are obtained by direct carbonization of tungsten powder. This process implies production of pure highly dispersed powder of metal tungsten within the first stage. The initial material in this case is very pure WO₃, tungsten acid or ammonium tungstate [7-9].

The second stage includes carbonization of tungsten by carbon in the graphite furnace with hydrogen atmosphere. Depending on the type of the furnace, atmosphere, and carbon content the reaction occurs according to the scheme:



or



The obtained tungsten carbide powder has particles of the indefinite melted form, minimum 3 – 5 μm in size and contains 5 % of W_2C minimum. The reduction terms greatly influence the characteristics of the metal powder and forming carbide.

Thermochemical synthesis of nano-phased tungsten carbide powders was also studied. It consisted of two stages [10, 11]. At first, nano-phased powders of metal tungsten were synthesized by reduction of various tungsten salts and chemical decomposition of vapor of volatile tungsten compounds. Then nano-phased tungsten carbide with the particle size of ~30 nm was obtained by carbonization at low temperature in the medium of controlled active carbon-containing gas phase.

The method suitable for tungsten carbide synthesis at low temperatures (~800°C) during 2 hours was suggested [12]. It is based on the gas-solid reaction between a tungsten source (ammonium paratungstate or tungsten oxide) and carbon-containing gas phase which includes a mixture of H_2 and CH_4 .

The conventional calcination–reduction–carburization (CRC) process offers the potential to manufacture commercial tungsten carbide powders with median grain sizes below 0.5 μm (ultrafine grades) [13].

In [14] point to that transferred arc thermal plasma method is more economical and less energy intensive than the conventional arc method and results in a fused carbide powder with higher hardness. Coatings of high wear resistance can be produced using fused tungsten carbide powder with WC and W_2C phases, which can be economically synthesized by thermal plasma transferred arc method [14].

However, it is not economically efficient to use very pure and fine tungsten powder obtained from tungsten compounds at the stage of its reduction for producing a large quantity of tungsten carbide powder.

The existing economical and technological restrictions make the problem of the development of large-scaled cheap production of ultrafine and nanosized tungsten carbide powders very actual. Nowadays, a promising ecologically safe method, discovered in 1967 by academician A.G Merzhanov and his co-workers I.P. Borovinskaya and V.M. Shkiro – Self-propagating High-temperature Method (SHS) – is used for obtaining refractory compounds of high quality. This method combines a simple technology with low power consumption and allows obtaining products with regulated chemical and phase

composition and dispersion degrees. Therefore the possibility of application of SHS technology for preparing ultrafine and nanosized tungsten carbide powders represented practical interest.

2. Experimental

2.1. Self-propagating high-temperature synthesis (SHS)

The new scientific direction SHS was developed at the interface of three scientific fields: combustion, high-temperature inorganic chemistry and materials science. SHS is an autowave process analogous to propagation of the combustion wave with the chemical reaction being localized in the combustion zone propagating spontaneously along the chemically active medium [15, 16]. The essence of the process is occurrence of exothermic reactions at temperatures developing as a result of self-heating of the substance; the synthesis temperature is up to 4000°C, the temperature growth rate – 10^3 - 10^6 K/s, the combustion velocity – 0.1-10 cm/s.

Thorough fundamental investigations of the SHS process have proved that chemical transformation in combustion waves and product structure formation occur simultaneously with high velocity and at significant temperature gradients. These peculiarities of the process provide practically complete chemical transformation of the mixture and a specific structure of the combustion products. Application of SHS allows avoiding the main disadvantages of conventional technological processes – high power consumption, complicated equipment, low product output.

The extreme terms which are characteristic of SHS of chemical compounds affect chemical and phase composition of the products as well as their morphology and particle size [17, 18]. The experiments in product quenching by special cooling methods immediately after the combustion front propagation have proved that “primary” product particles of 0.1-0.2 μm in size can be formed in the combustion front [19, 20].

The product structure formation during the chemical reaction was called primary structure formation while the structure formed in this case was called the primary structure of the product. The characteristic time of the chemical reaction is 10^{-3} - 10^{-1} s; the time of the primary structure formation being the same. After the chemical reaction the particle size increases as a result of the secondary structure formation process followed by collecting recrystallization [21]. The duration of the process depends on the sample cooling mode and is usually about some or tens seconds.

Transformation of initial reagents to final SHS products is a complicated multiparametric process. There are various ways to govern it. The main types of the occurring processes are solid-flame combustion in the solid-solid system (one of the varieties is combustion with the intermediate melted layer), gas-phase SHS (chain flames, combustion of condensed systems with gaseous intermediate zone), combustion of solid-gas systems (filtration combustion, combustion of gaseous suspensions) [22].

Let us consider the possibilities of these processes.

In order to obtain ultrafine and nanosized products in the processes of solid-flame combustion, one must use the reagents of the same dispersion. In solid-phase systems with the intermediate melted layer the possibility of nano-crystal formation depends on crystallization and recrystallization processes, combustion heat modes and product cooling after the reaction.

In the case of gas-phase SHS (gas combustion followed by a condensed product formation) the product elemental particles consolidate with each other and form nuclei on the surface of which the following reactions occur. If fast artificial cooling is used, it is possible to arrest the particle size growth at a required stage and obtain nanopowders by depositing the particles from the gas mixture.

At gas-phase combustion the initial reagents, intermediate and final compounds remain in the condensed state (either liquid or solid) during the entire reaction [16, 23].

The SHS method has provided the possibility of obtaining a great number of compounds in the dispersed state (powder). Among the materials for which the technological backgrounds are well developed the main ones are powders of refractory compounds. They are widely used in industry due to their outstanding properties such as hardness, thermal stability, abrasive wear and resistance.

There are several directions of the SHS technologies. The widest and well-developed type of SHS reactions is the synthesis reactions of refractory compounds from elements. It is oxygen-free combustion. Both powders and gaseous elements take part in the chemical reactions. Besides, some regulating additions R are introduced into the initial mixture. They can be synthesis products (as diluents), various inorganic and organic compounds.

Another direction is combination of SHS with thermal reduction (SHS with a reducing stage) when the compounds of elements (oxides, halogenides, etc.) and metal-reducers – Mg, Ca, Al, Zn, etc. are used for the synthesis. The advantages of this method are a low price and availability of raw materials. Besides, metallothermic powders are characterized by such valuable properties as high dispersion and homogeneous granulometric composition.

The interaction of the reagents in the combustion wave occurs within two stages. The first one (reduction of the main metal oxide) is a metalthermal reaction. The second stage (SHS itself) is the interaction of the reduced metal with a non-metal followed by a refractory compound formation. There are a lot of secondary reactions which should be suppressed when optimum technological terms of the process are worked out. In the complicated systems of oxide – metal-reducer – carbon (hydrocarbon), carbon-containing components take part in carbide formation and reduction of metal oxides as well. It defines the requirements to the choice of the initial components ratio.

As a result of the SHS with a reducing stage a “semiproduct” is obtained which contains the main compound and the secondary products which can often be metal-reducer oxides. In metallothermic powders the secondary product is distributed uniformly in the whole

volume of the reactive mass. So it is necessary to carry out some additional operations to sort out the main compound [24, 25].

Having analyzed the literature data, we can conclude that in the case of the development of the SHS technology of tungsten carbide the main attention should be paid to detection of the terms of nano-particle formation during the synthesis process. However, investigation of the separation methods of chemically pure ultrafine and nanosized compounds from the synthesis products and their analysis are very important too.

2.2. Chemical dispersion

SHS products are cakes or ingots which should be processed for obtaining powders. It can be achieved by either mechanical milling or chemical treatment.

Mechanical milling (conventional milling by balls, friction milling, planetary milling) is the easiest method for obtaining ultrafine and nano-sized powders. It is possible to obtain fine powders (up to 10-20 nm), but the problems of the long duration of the process, powder contamination with the ball and vessel materials, high power consumption require some additional solution.

One of the promising methods of obtaining nano-sized powders is the method microparticle dissolution. Recently, the efficiency of the dissolution processes for converting microparticle size to the nano-level has been confirmed. The method is based on the property of particles to decrease their volume uniformly due to their dissolution in acid and alkali media. But simultaneously the structure and the properties of the central part of the substance or phase remain the same [26].

The main aim of powder application is to obtain a dense product with homogeneous microstructure after compaction. The common reason restricting the refractory material strength is existence of agglomerates in the powder [27]. So in order to make the powder strong, it is necessary to disintegrate or remove large solid agglomerates from the initial powder. In the case of ultrafine powders the agglomerates are disintegrated by dispersing and milling in suitable solutions.

The influence of various solutions on the powder structure, dispersion degree and specific surface area has been already studied for SHS powders of boron nitride and aluminum nitride.

After synthesis, the materials were mechanically disintegrated and subjected to thermochemical treatment in neutral, acid, and alkali media at temperatures ranging from 20 to 100°C [28]. Such treatment is termed "chemical dispersion" of SHS products, as suggested by Merzhanov [29]. Chemical dispersion in a neutral medium resulted in increased total, outer, and inner specific surfaces. Mean grain size decreased. This implies that chemical dispersion provided for disintegration of the materials, as well as leading to formation of new channels and pores and the appearance of new defects, finally resulting in improved specific surface.

In [25] describes thoroughly the application of chemical dispersion for separating ultrafine and nanosized powders of boron nitride obtained by various methods under the SHS mode: from elements, with participation of boron and boron oxide, and from boron oxide with the stage of magnesium reduction.

Possible production of tungsten carbide of ultrafine and nanosized structure by the SHS technology with a reducing stage with using chemical dispersion for separation of submicron powders was of great practical interest.

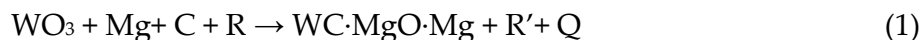
This paper demonstrates the investigation results of the dependence of SHS tungsten carbide powder dispersion on the SHS process parameters and composition of the solutions used for chemical dispersion of the synthesis products and separation of the final product. The aim is producing single phase tungsten carbide with ultrafine and nanosized structure.

2.3. Experiment description and products characterization

The starting materials used were 99,98+%-pure WO_3 with an average particle size of 10-12 μm (commercially available material which is used in the production of hard alloys), P804-T furnace black less than 45 μm in particle size, and I.PF-1 magnesium powder (99.1+%) ranging from 0.25 to 0.50 mm in particle size.

To mix the components and grind the SHS products, we used ball mills with steel grinding media. Synthesis was carried out in a 30-l SHS reactor under argon atmosphere.

To prepare tungsten carbide, we used the exothermic reaction between tungsten oxide, carbon (black), and magnesium metal:



where R is a regulating additive.

The temperature of this process exceeds 3000°C; it can cause decomposition of the forming tungsten carbide. To reduce the combustion temperature, we introduced different additives, inert or decomposing in the combustion wave to form gaseous products. The unstable additives also acted as dispersants ensuring a small particle size of the SHS products.

In addition to tungsten carbide and magnesia, formed in the oxidation-reduction reaction, X-ray diffraction revealed some amount of unreacted magnesium in the intermediate product and also intermediate compounds (magnesium carbides) formed in the synthesis (**Figure 1**).

According to the chemical analysis magnesium content in water-soluble compounds (it should be related to forming carbides) is 0.7 – 0.9 mass %, metal magnesium (unreacted) is 15-17 mass %. The study on the semiproduct microstructure has proved, that ultrafine crystallites of tungsten carbide appear to be embedded into the amorphous phase of the melts of magnesia and metal magnesium (**Figure 2**).

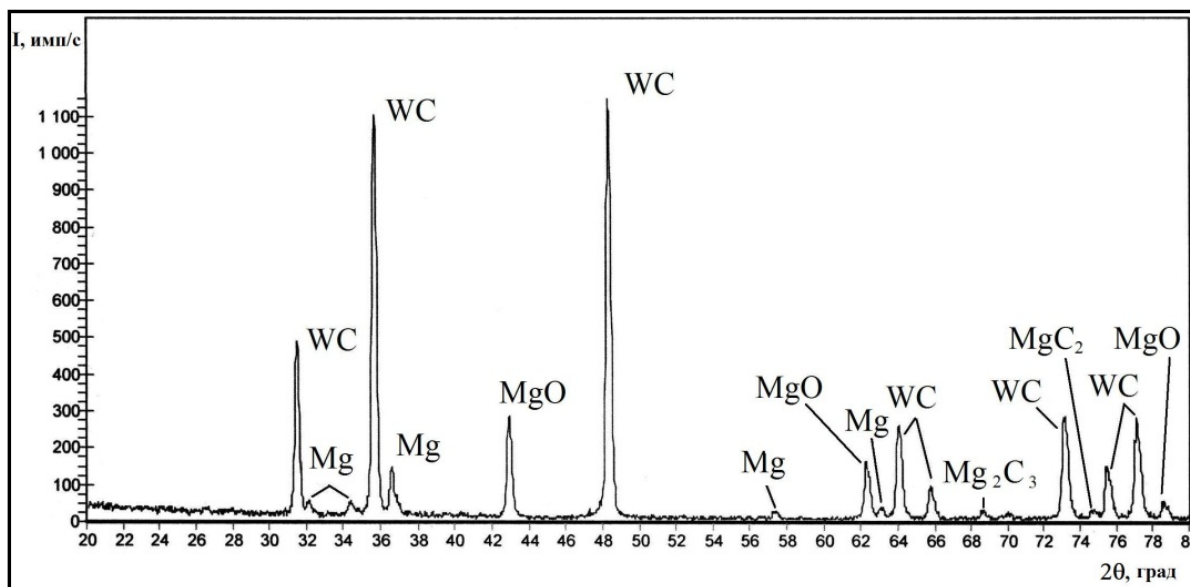


Figure 1. X-ray pattern of WC·MgO·Mg intermediate product.

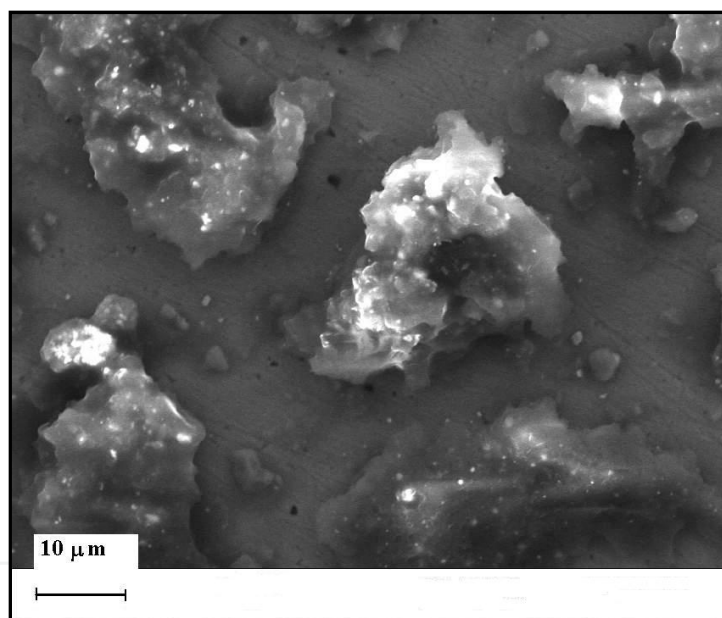


Figure 2. Microstructure of WC·MgO·Mg intermediate product.

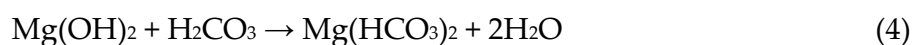
The process of chemical dispersion in various solutions is necessary for separation of the target products from the cakes forming during SHS and their further purification from admixtures with simultaneous change in the obtained powder dispersion.

The milled cake was treated with water solutions of hydrochloric acid (1:1) or sulfuric acid (1:5) (acid enrichment) for tungsten carbide separation from the semiproduct. Unreacted metal magnesium and magnesium oxide which was formed during the synthesis process were dissolved.

At first the powder was treated by chloride solutions since it is known that water solutions of haloid salts destroy metal magnesium. Magnesium, potassium and ammonium salts were

chosen. It was carried out in order to avoid active gas release when the milled cake was treated with diluted acid solutions (hydrogen release during the interaction of unreacted magnesium with acids) as well as to decrease acid consumption for acid enrichment of the synthesized product.

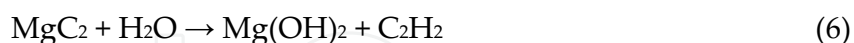
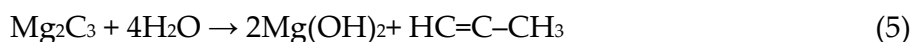
For decreasing acid consumption, the pulp, consisting of WC·MgO·Mg semiproduct and some amount of magnesium chloride as a catalyst, was saturated with carbon dioxide. During this treatment magnesium content in the solid residue was decreased and in the solution it was increased. Metal magnesium is supposed to transform to solution in the following way:



At first the pulp is prepared. It is suspension of the treated powder in water. Then the required amount of the acid equal to the stoichiometric ratio is introduced. The addition of water to WC·MgO·Mg is followed by active gas release and the solution heating though distilled water is not supposed to affect metal magnesium greatly due to $\text{Mg}(\text{OH})_2$ film appeared on magnesium particle surface [29].

It is known, that at 500°C , MgC_2 can be formed; this carbide is easily disintegrated by water to form acetylene. As the temperature grows from 500 to 600°C , carbon is separated from MgC_2 and Mg_2C_3 appears; this carbide being typical for magnesium only. Methyl acetylene releases during Mg_2C_3 hydrolysis.

So the following reactions can occur in the water solutions:



Infrared spectroscopy was used to analyze the gases released in the reaction of WC·MgO·Mg intermediate product with chloride solutions (**Table 1**).

When the intermediate products are treated with potassium chloride and ammonium chloride solutions, a great amount of methane, acetylene, and methyl acetylene is released. It proves the supposition of magnesium carbide formation during SHS. Existence of some amount of methane in the gaseous mixture can be explained by hydrolysis occurring on tungsten carbide particle surface. More gas will be released if ammonium chloride solution is used due to the fact that ammonia is formed during hydrolytic decomposition.

The secondary compounds were removed completely due to the powder treatment with acid solutions

Reactive system	Gas volume, cm ³	Concentration of substance in gas phase, mg/m ³		
		CH ₄	C ₂ H ₂	C ₃ H ₄
WC·MgO·Mg +KCl+H ₂ O	292	16.0	3.1	12.3
WC·MgO·Mg+NH ₄ Cl+H ₂ O	405	14.8	1.4	7.2

Table 1. Gas release at WC·MgO·Mg treatment with salt solutions

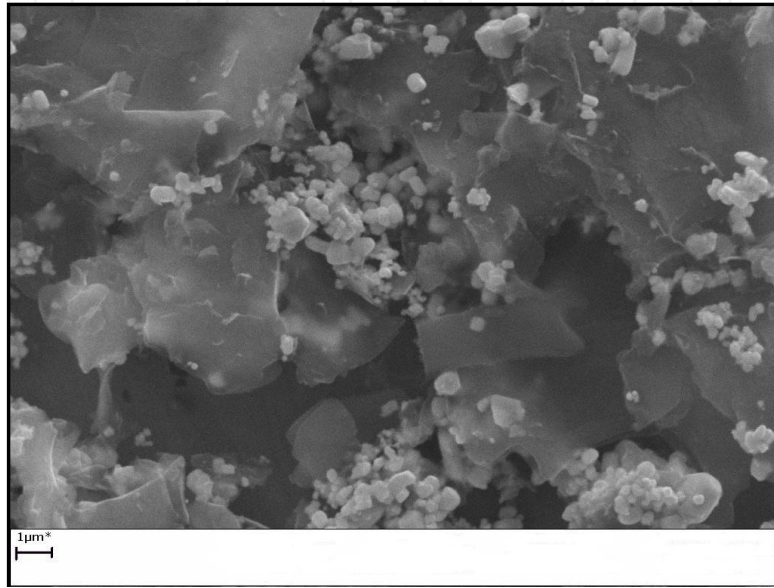


Figure 3. WC-C powder separated from WC·MgO·Mg semiproduct by acid enrichment

Microstructure analyses (**Figure 3**) have shown, that the tungsten carbide powders resulting from acid enrichment represented large accumulations of fine particles of the main product and unreacted (free) carbon. The chromium mixture (10 g K₂Cr₂O₇ in 100 ml H₂SO₄) oxidizes graphite and amorphous carbon at $T \leq 180^\circ\text{C}$. Preliminary research showed that the treatment of tungsten carbide powder with chromium mixture solution at $T \leq 180^\circ\text{C}$ allowed removing free carbon without dissolving the main product. The carbide powders resulting from acid enrichment were refined with chromium mixture.

As a result, the content of free carbon decreased from 1.0-5.0 to 0.02-0.2%, while the content of oxygen increased due to oxidation of tungsten carbide particle surface. Tungsten carbide particles appeared to be covered by acicular tungsten oxide crystals, which are easily dissolved in diluted alkaline solutions (**Figure 4**).

The changes in the phase and elemental composition of tungsten carbide powder as a result of chemical dispersion in chromic acid mixture and alkaline solutions are presented in **Table 2**.

X-ray diffraction analysis proved that the final products contained only one phase of tungsten carbide. Chemical dispersion in various media caused the primary agglomerates to disintegrate into finer structures of hexagonal tungsten carbide (**Figure 5**).

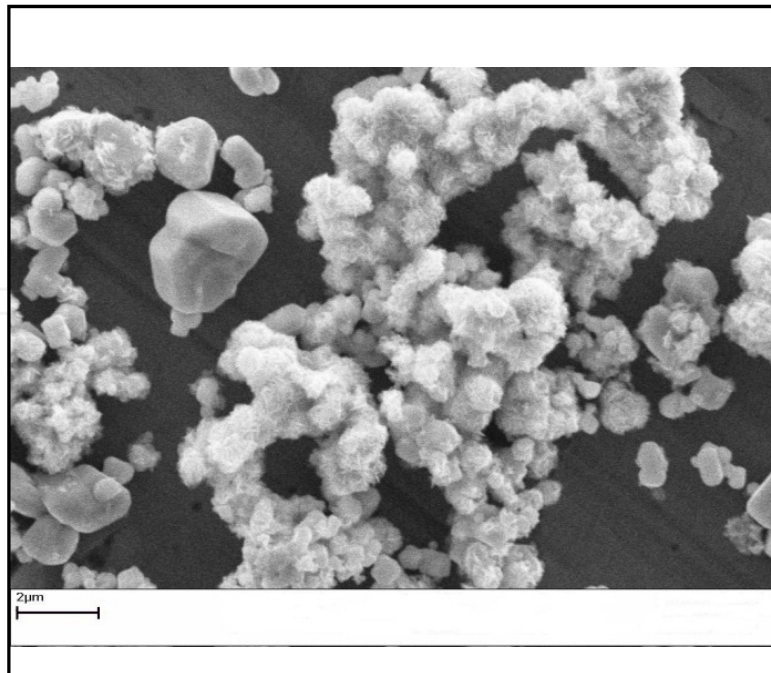


Figure 4. Microstructure of oxidized tungsten carbide powder

Dispersion solution	Dispersion time, h	Weight percent				
		C _{total}	C _{free}	Mg	O	Cr
H ₂ SO ₄ (1:4)	3,0	7,97	2,05	0,063	0,16	
5% K ₂ Cr ₂ O ₇ in H ₂ SO ₄ (conc)	3,0	6,12	0,03		0,24	
Aqueous 1% KOH	0,5	6,13	0,03	0,005	0,03	0,005

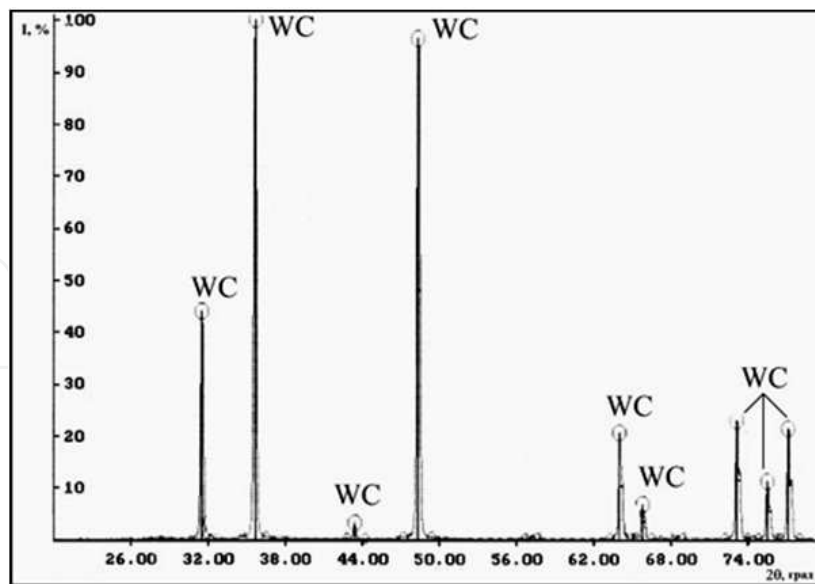
Elemental analysis of WC·MgO·Mg semiproduct: W_{total} = 44.1 %; C_{total} = 4.1 %; Oxygen = 9.3 % Mg_{acid.sol.} = 37.7 %; Mg_{metal} ~ 15.7 %; Mg_{water sol.} = 0.8 %

Table 2. Effect of chemical dispersion on the elemental composition of tungsten carbide powder

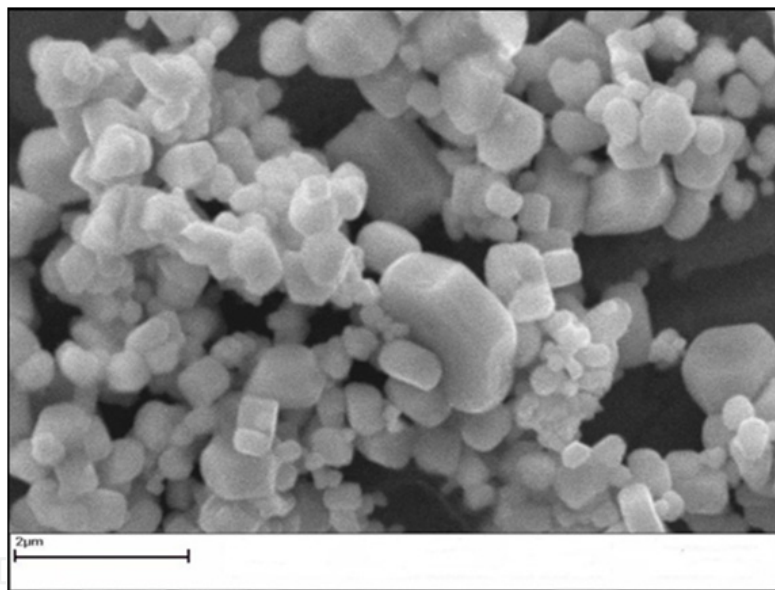
3. Results and discussion

The study on SHS stages and chemical dispersion has proved that the final dispersion of the target tungsten carbide product depends on various factors. It was established that the initial mixture composition and density, reactant ratio, their aggregative state in the combustion area, gas pressure, and the nature of regulating additives influenced the size of powder particles.

When calcium chloride or hydride as well as ammonium chloride are used as regulating additives, the final product contains two phases WC and W₂C. When the mixture of ammonium chloride and high-molecular polyethylene or that of metal magnesium and WC·MgO·Mg semiproduct are used, the single-phase target product is obtained.



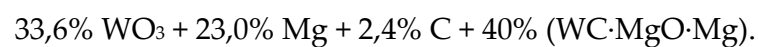
(a)



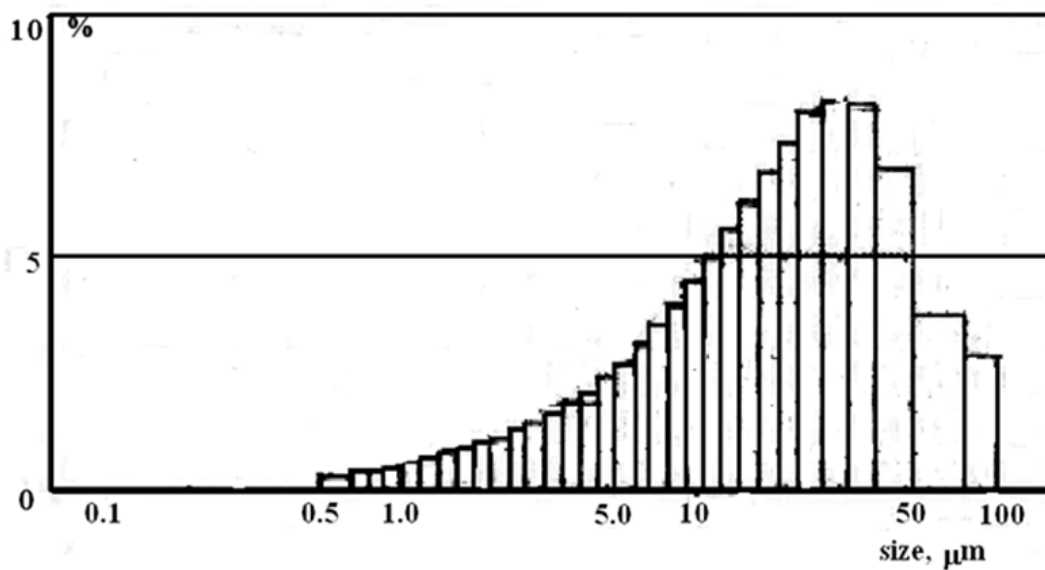
(b)

Figure 5. X-ray pattern (a) and microstructure (b) of purified tungsten carbide powder.

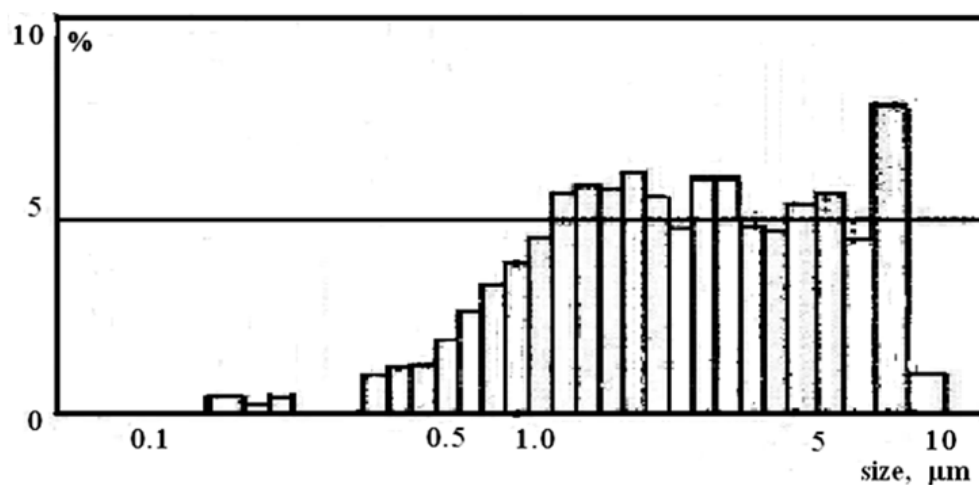
The carbon content influenced the phase composition of the product (W_2C content). The single phase product WC is formed in the case of the following ratio of the initial components in the green mixture:



The content of magnesium in the starting mixture has a substantial effect on the size of carbide particles: the stoichiometric amount of magnesium results in coarse powders, while it excess leads to a fine product (**Figure 6**).



(a)



(b)

Figure 6. Particle size distributions in tungsten carbide powders: (a) stoichiometric amount of magnesium in the starting mixture, (b) excess of magnesium in the starting mixture.

The excess of magnesium in the mixture seems to inhibit the growth of tungsten carbide crystals and to form a liquid phase when carbides are crystallized; the liquid phase and adjusting additives prevent intensive crystal growth. Introduction of $WC \cdot MgO \cdot Mg$ into the green mixture also decreases the dispersion degree of the final product. Probably, the introduced additives as well as metal magnesium form a liquid phase under the terms of crystallization. Tungsten carbide ultrafine crystals contained in the introduced semiproduct can accelerate tungsten carbide crystallization and appear to be crystallization centers but a rather viscous medium prevents intensive crystal growth. Coating of tungsten carbide particles with liquid melt results in better stability of tungsten carbide to hydrolysis and oxidation after the synthesis process.

In studying chemical dispersion, the above results were used to analyze how the composition of the solutions, used to recover tungsten carbide from synthesized products, influenced the structure and particle size of the final tungsten carbide powders. The following systems were used:

- diluted sulfuric acid (1 : 5),
- diluted hydrochloric acid (1 : 1),
- ammonium chloride and hydrochloric acid solutions,
- potassium chloride and hydrochloric acid solutions.

It was established, that the tungsten carbide particle size depends on the composition of solutions used at the first chemical dispersion stage: recovery of carbide from intermediate product (**Table 3**).

Acid enrichment conditions	Volume fraction, %	
	≤ 300 nm, %	≤ 500 nm, %
HCl (1:1)	61,3	87,5
H ₂ SO ₄ (1:5)	66,7	86,3
30 %NH ₄ Cl + HCl	81,6	96,5

Table 3. Fraction volumes of refined tungsten carbide powders with minimum particle sizes.

This result can be explained by the following way. Tungsten carbide is thermodynamically unstable and can be oxidized in the medium of water or oxygen at the room temperature [30]. X-ray phase analyses of tungsten carbide powder state in the humid medium show, that the surface of tungsten carbide particles is the first to be oxidized. The thickness of the oxide film increases with an increase in humidity [31].

In water the oxide film is entirely removed due to its dissolution and formation of tungstate-ions by the reaction:



When the milled semiproduct is dispersed by ammonium chloride or potassium chloride solutions, the pH of solution changes from low acid values to high alkali ones. The forming medium provides acceleration of oxide film dissolution by Reaction 8 and deeper tungsten carbide particle hydrolysis leading to a decrease in the particle size due to dissolution from the surface. So, chloride application at the stage of acid enrichment allows obtaining tungsten carbide powder with the number of particles of less than 300 nm in size being 80 % of the total number (**Figure 7**). Using suitable emulsifiers can disintegrate the agglomerates and separate tungsten carbide particles of less than 100 nm from ultrafine ones.

Application of ultrasound in the process of chemical dispersion decreases the time of the process and affects the dispersion degree of the product. In the case of mechanical mixing refining of tungsten carbide powders with chromium mixture takes several hours. The

ultrasound effect decreases the time to 30 – 40 minutes. It can be explained by disintegration of tungsten carbide agglomerates and carbon coarse particles and acceleration of the reduction-oxidation reaction of chromium mixture with free carbon.

The ultrasound effect on tungsten carbide composition and dispersion has been studied (**Table 4**).

Refinement time	Refinement temperature	C _{total} , mass %	C _{free} , mass %	Oxygen, mass % (non-purified product)	Oxygen, mass % (purified product)
30 min	145°C	5,72	0,015	1,40	0,14
45 min	85°C	5,18	0,013	2,35	0,07

Table 4. Ultrasound effect on tungsten carbide powder composition at final product refinement

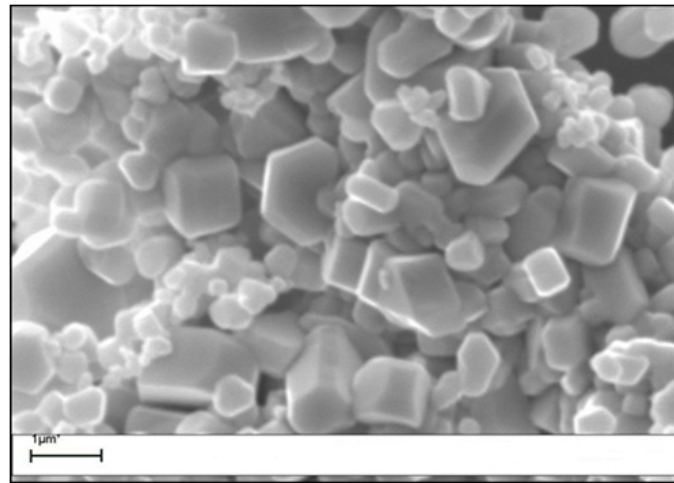
After refining with chromium mixture, the carbon content decreases to ~0.1 % but oxygen content increases greatly (in comparison with mechanical mixing) due to oxidation of tungsten carbide particle surface. The lower the refinement temperature and the higher time of ultrasound action are used, the higher dispersion of tungsten carbide powder is achieved (**Figure 8**). Under these terms the process of tungsten carbide particle surface oxidation is more active; therefore the particle size is actively decreased (powder A). An increase in the refinement temperature results in obtaining less dispersed powder B due to dissolution of fine particles under the strict terms of the process.

The powder (**a**) consists of agglomerates of fine and coarse particles. It is possible to separate ultrafine and nanosized tungsten carbide particles using proper technological terms. In the powder (**b**) fine tungsten carbide particles are situated on the surface of coarser particles and it makes their further separation much more difficult. Therefore, the ultrasound application results in additional milling of tungsten carbide powders and more complete purification from admixtures.

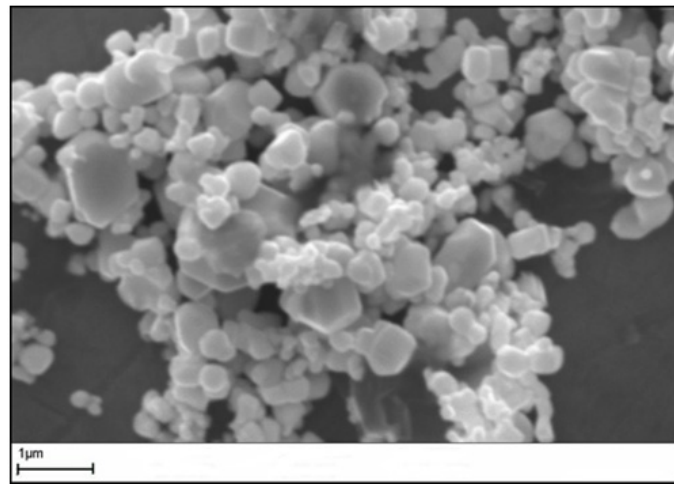
The results of the work on SHS of tungsten carbide powder with the reduction stage led to the development of the industrial technology of ultrafine and nanosized tungsten carbide powders synthesis. **Figure 9** demonstrates the curve of the particle size distribution of tungsten carbide powder synthesized in the industrial reactor. Obviously, the product is a mixture of particles of different sizes. The prevailing particles are ultrafine and nanosized ones.

Tungsten carbide powders synthesized by the developed technology were tested in making alloys and items thereof.

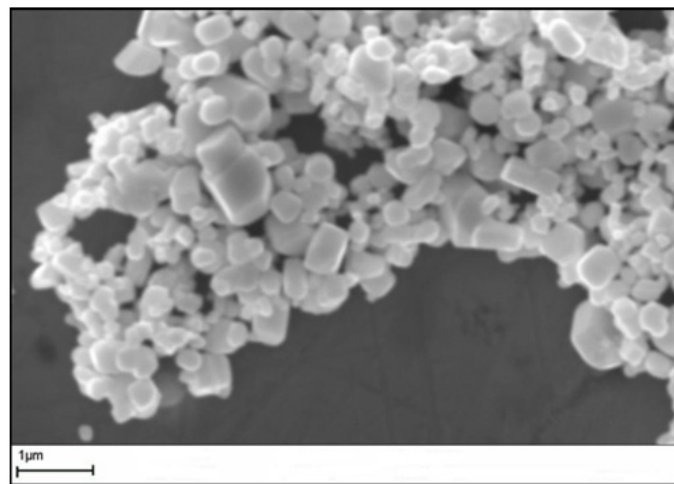
We studied sinterability of fine-particle of SHS tungsten carbide powders. **Table 5** compares the physicochemical properties and structure of WC-Co alloy prepared with the use of SHS tungsten carbide and the commercial alloy VK6-OM (containing tungsten carbide produced by a furnace process).



(a)



(b)



(c)

a - HCl (1:1); **b** - NH_4Cl (30 % solution) + HCl (1:1); **c** - KCl (30 % solution) + HCl (1:1)

Figure 7. Tungsten carbide powder microstructure depending on the terms of acid enrichment

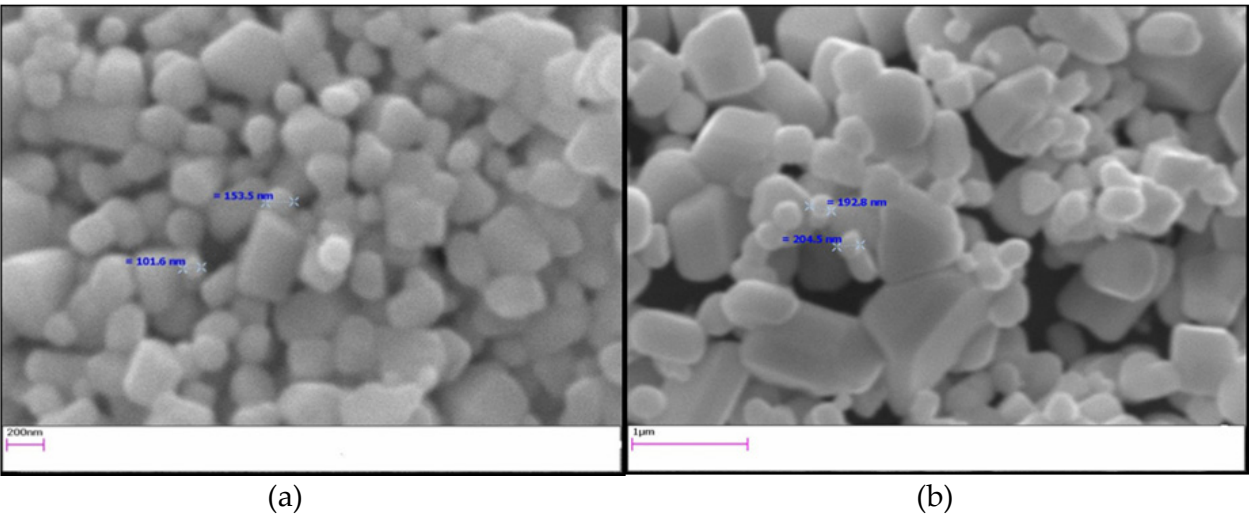


Figure 8. Dependence of refined tungsten carbide powder microstructure on the terms of ultrasound treatment: A – T=85°C; B – T=145°C.

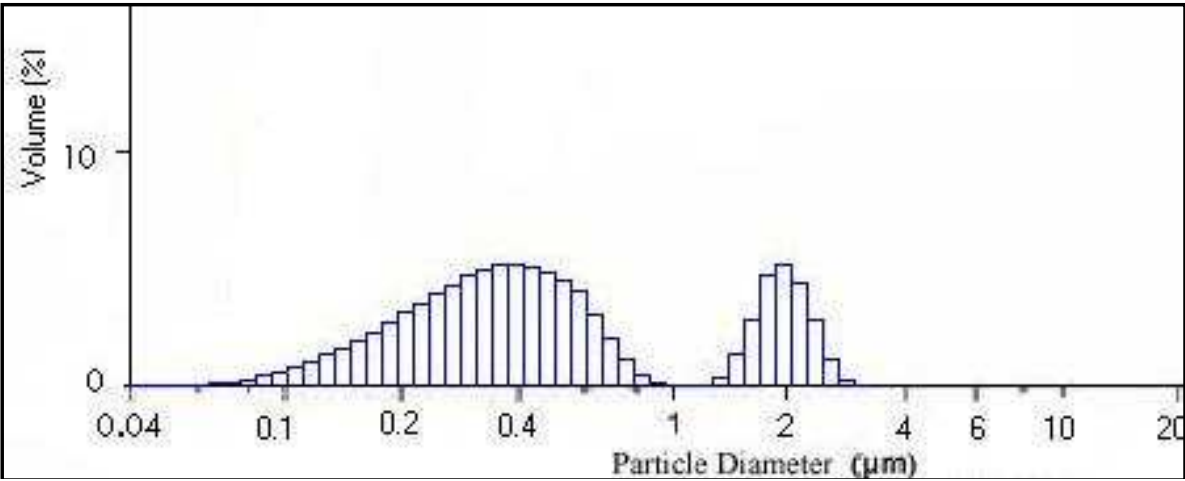


Figure 9. Particle size distribution of tungsten carbide powder synthesized in industrial reactor.

Parameters	SHS WC alloy	VK6-OM alloy (standard)
Density, g/cm ³	14.9	14.7
Hardness, HRA	91	90.5
Coercivity, A/m	270	280
Bending strength, σ , kg·f/mm ²	170	130
Durability coefficient	1.4	1.0
Porosity, A %	0.04	0.2
Percentage of particles less than 1 μm in size	80 %	60 %

Table 5. Physicochemical properties of WC-Co alloys prepared by using WC-SHS and WC-furnace process.

The bending strength, durability coefficient, and dispersion degree of the alloy produced from SHS tungsten carbide exceed those of the commercial alloy.

As a result of the realized research, the technology of Self-propagating High-temperature Synthesis has been developed and is being introduced for production of ultrafine and nanosized tungsten carbide powder with the use of chemical dispersion for separation, purification and additional milling of the target product.

Organization of industrial SHS production of submicron tungsten carbide powders includes:

- development of hydrometallurgical stage of submicron tungsten carbide powder separation;
- development of the production line with complete or partial automation;
- organization of design work in modernization of non-standard equipment and in selection of standard additional devices;
- preparation of the workshop for tungsten carbide semiproduct treatment (leaching, utilization and regeneration of wastes).

The annual production output is 150 tons. The profitableness is up to 80 %.

4. Conclusion

The processes of Self-propagating High-temperature Synthesis were studied for obtaining nanosized powders of refractory compounds, particularly, tungsten carbide. The SHS terms influence crystallization of the obtained powders. Varying the SHS parameters (reactant ratio, regulating additives, inert gas pressure, combustion and cooling velocities) allows changing tungsten carbide powder morphology and particle size.

SHS tungsten carbide powder differs from its furnace and plasmochemical analogs in structure and purity. The grain size can be governed during the SHS processes. Powders of less than 100 nm in particle size can be obtained at complete suppression of recrystallization in combustion products. Separation of the powders from the milled cakes by chemical dispersion with various solutions and choice of chemical dispersion terms (the solution composition, the process time and temperature) allow obtaining SHS materials with the nanostructure characterized by high specific surface area and particle size less than 100 nm with simultaneous preserving the phase and chemical composition of the product.

As a result of the realized research, the technology of Self-propagating High-temperature Synthesis has been developed for production of ultrafine and nanosized tungsten carbide powder with the use of chemical dispersion for separation, purification and additional milling of the target product. The sinterability of the synthesized tungsten carbide powder was studied. The bending strength, durability coefficient, and dispersion degree of WC-Co alloy produced from SHS tungsten carbide exceed those of the commercial alloy.

The proposed technology of ultrafine and nanosized tungsten carbide powder synthesis has some advantages in comparison with the available technologies:

- Availability of theoretically explained backgrounds for governing the reaction temperature and velocity and component conversion completeness, which provide the possibility of obtaining high quality products of the preset structure at optimum terms;
- Low requirements to the initial mixture quality since partial self-purification of SHS products from admixtures takes place during the combustion process;
- Simple equipment using various approaches of physical influence on the substance;
- Possibility of industrial production of nanosized materials.

Nowadays, the number of ultra-dispersed materials produced in industry is restricted. Development of industrial production technologies and widening of application fields of nanosized materials is commercially important.

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