# ELECTRIC DISCHARGE METHOD OF OBTAINMENT OF TITANIUM CARBIDE HARD METALS

## ЭЛЕКТРОРАЗРЯНЫЙ МЕТОД ПОЛУЧЕНИЯ КАРБДОТИТАНОВЫХ ТВЕРДЫХ СПЛАВОВ

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**Abstract:** *A complex approach to obtainment of titanium carbide hard metals, which consists of utilization of high density energy flows of high voltage electric discharges (HVED) for dispersion and activation of particles of powders mixture of 80 % Ti + 20 % Fe composition and synthesis of carbide phase and subsequent consolidation of obtained powders mixture by high density electric current with spark plasma sintering (SPS) method. Connection between specific cyclic energy of treatment of "kerosene – Ti + Fe powders mixture" disperse system and changes of dispersity, shape and phase composition of powders and physical and mechanical properties (hydrostatic density, hardness, thermal conductivity, wear resistance, dynamic strength) of materials consolidated from them is found. Tungstenless titanium carbide hard metals, which have high specific values of strength and wear resistance, hardness of which is higher than 82 HRA, and thermal conductivity of such materials is insignificantly lower than thermal conductivity of VK6 alloy, were obtained.*

***KEYWORDS:*** *HIGH VOLTAGE ELECTRIC DISCHARGE, HARD METAL, TUNGSTENLESS HARD METAL, POWDER, FUNCTIONAL PROPERTIES, DISPERSION, SYNTHESIS, SPARK PLASMA SINTERING*

## 1. *Introduction/Введение*

Currently attention of scientists is directed at development and implementation of hard metals (HM) that do not contain tungsten – tungstenless hard metals (TLHM), which usually also do not contain Cobalt, which is substituted by Nickel or Ferrum [1, 4–5]. Development of TLHM is concentrated on the creation of material based on complex Titanium-Niobium carbide with Nickel-Molybdenum matrix (TM type), Titanium carbide with Nickel-Molybdenum matrix (MNT, TN, NTN etc.), Chromium carbide with Nickel matrix, Titanium carbide and carbonitride with steel matrix (carbide steels, ferroticars) and HB on non-carbide base (cermets etc.). For all of the above except case of using Titanium carbide and carbonitride with steel matrix, complexity and expensiveness of materials production take place. At the same time, TLHM if compared to conventional tungsten-containing hard metals usually have lower elastic modulus, lower thermal conductivity and toughness, thus they are worse at resisting shock and thermal loads, elastic and plastic deformations, have lower high-temperature strength, they suffer more intensive loss of strength at high temperatures, have increased abrasive wear on back surface of cutting tool. It is worth noting that usage of TLHM as a substitution for tungsten-containing HM does not lead to any significant technic or economic impact [1, 4–6].

There is an approach which allows increasing physico-mechanical and performance properties of materials, which can be applied during preparation of powder mixtures for consolidation during production of TLHM. It consists in using high voltage electric discharge (HVED) in liquid which can purposefully impact phase and disperse composition of powders, Fe–Ti system mixtures in particular which leads to an increase of functional properties of material consolidated from them [7–14]. Theoretical evaluation based on thermodynamic analysis as well as experimental studies confirmed changes of phase composition of Ferrum and Titanium powders mixtures under the impact of HVED in hydrocarbon liquid. In work [14] it is shown that HVED leads to destruction of hydrocarbon liquid by plasma discharge channel and synthesis of nanocarbon and hydrogen; also HVED leads to intensification of passage of reactions between powder mixture components and products of hydrocarbon liquid decomposition which leads to synthesis of Titanium ad Ferrum carbides and intermetallic compounds. Technology of HVED impact on powder mixtures of Ferrum, Titanium and Boron carbide in hydrocarbon liquid was successfully applied by authors of present work for obtainment of powder mixtures for production of carbide steels [15]. Combination of powders HVED treatment and subsequent spark-plasma sintering (SPS) of synthesized powder mixtures allowed preservation of fine grain structure of compact and ensuring an increase of physico-mechanical properties of carbide steel [10, 12].

**The goal** of present work is the determination of connection between cyclic specific treatment energy on "kerosene – Ti + Fe powder mixture" disperse system and changes of dispersity, shape and phase composition of powders and functional properties of hard metal materials consolidated by SPS.

## 2. *Preconditions and means for resolving the problem/Предпосылки и средства для решения проблемы*

Powder mixture of 80 % Ti + 20 % Fe composition was treated by HVED. Treatment of suspensions of Titanium powders of PT 6 TU U 14-10-026-98 (ПТ 6 ТУ У 14-10-026-98) brand and Ferrum powders of PZhR 3.200.26-30 GOST 9849–86 (ПЖР 3.200.26-30 ГОСТ 9849–86) brand in kerosene of TS-1 GOST 1022–86 (ТС-1 ГОСТ 10227–86) brand was performed in working chamber, scheme and detailed description of which are given in [7, 12], Parameters of HVED treatment were selected according to works [7–14], and specific treatment energy $W_s$ of "kerosene – Ti + Fe powders mixture" disperse system varied in range from 4.5 to 27 MJ/kg by changing pulses quantity.

Metallographic analysis by digital photographs, made on optical BIOLAM-I (БИОЛАМ-И) microscope and raster electron microscope REMMA-102 (РЭММА-102), was used in order to evaluate the impact of HVED treatment on morphology and dispersity of particles according to GOST 23402–78 (ГОСТ 23402–78). Samples of powder for microscopy were taken according to ISO 3954–77. Differential curve of powder particles diameter distribution by their quantity $F_d(d) = \mathrm{d}F/\mathrm{d}D$ was built by differentiating integral cumulative curve, smoothing was performed using the method of consecutive application of the moving average with the window of two points with previous division into intervals of 0.05 μm size. Studies of powders phase composition were performed by X-ray diffraction analysis method. Registration of X-ray diffractograms was performed using Rigaku Ultima IV X-ray diffractometer at CuKα radiation. Identification of phases on X-ray diffractograms was performed using QualX [16] software. Powders bulk density was determined according to ISO 3923-1–79 using funnel.

Sintering of powders was performed on "Gefest-10" experimental SPS complex with maximal amplitude of AC and DC superposition of 1.1 kA, frequency of AC component of 10 kHz, input sintering energy during 1 s, which is numerically and physically equal to sintering process power, of 7.5 kJ/s, temperature rise rate of 20 °C/s and holding time of 270 s (total time) wile mechanic pressure of loading was 60 MPa according to works [10, 11].

Density of consolidated specimens was determined by hydrostatic weighting in ethylene according to ISO 3369–75. Hardness of specimens was studied according to ISO 3738/1–82 on TP 5006 hardness meter. Dynamic strength was studied using specimens compression diagram on experimental stand for dynamic tests according to Hopkinson method [17]. Specimens wear resistance was determined by weighting method on SMC-2 (СМЦ-2) friction machine with "roller-block" scheme at dry friction (without lubricant) [18]. Immobile cylindrical specimen (block) and counter-body (roller) – movable flat diamond circle of direct profile of 1A1 F50×16×3×16 AS4 (1A1 Ф50×16×3×16 АС4) brand with 160/80 grain according to GOST 16167–90 (ГОСТ 16167–90) were the friction pair. Peripheral speed of roller was 0.8 m/s, pressure on specimen was 0.75 MPa. Pre-grinding of contact surfaces was performed before the tests. During studies, specimens were weighted after every 0.5 km of way. Thermal conductivity of "glass – specimen" system was determined on thermal conductivity meter IT- λ-400 (ИТ-λ-400) according to [19]. Organic glass according to GOST 17622–72 (ГОСТ 17622–72) with thickness of 0.8 mm was used during studies, because thermal conductivity of specimens was too high for studies on mentioned instrument.

## *3. Results and discussion / Результаты и их обсуждение.*

Microscopy studies of morphologic characteristics have shown that initial 80 % Ti + 20 % Fe powder mixture size was from 0.5 to 160 µm (see Fig. 1, curve 1). Median of distribution was ~ 43 µm and mean diameter was 37.5 µm.

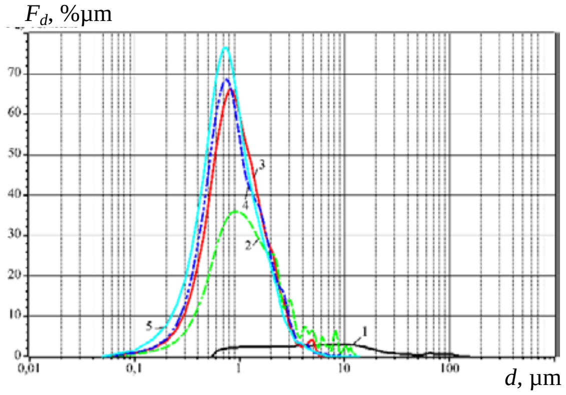


***Fig. 1*** *Differential curves of quantity distribution of diameter of 80 % Ti + 20 % Fe powder mixture by size*
*1 – before HVED treatment; 2 – after HVED treatment with specific energy of 4.5 MJ/kg;3 – after HVED treatment with specific energy of 9 MJ/kg; 4 – after HVED treatment with specific energy of 18 MJ/kg; 5 – after HVED treatment with specific energy of 27 MJ/kg*

HVED treatment of powders with specific treatment energy of 4.5 MJ/kg leads to significant change of powder mixture dispersity (see Fig. 1, curve 2), particle size is in range from ~ 0.1 µm to 13.5 µm while median of distribution is 2.2 µm and mean diameter is 3,2 µm. Peak diameter value is 1 µm and 36 %.

Increase of specific treatment energy to 9 MJ/kg (see Fig. 1, curve 3) leads to further changes of particles size – their size range is from ~ 0.1 µm to 12.5 µm, median of distribution is 1.3 µm and mean diameter is 1.6 µm, Peak diameter value is 0.8 µm and 66 %.

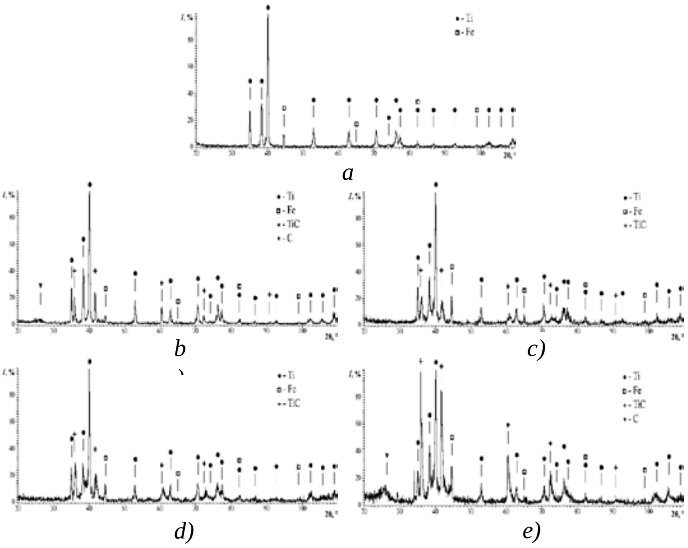
Further two times increase of specific treatment energy to 18 MJ/kg leads to decrease of dispersion dynamics, powder particles are grinded to sizes from ~ 0.1 µm to 6.5 µm, while median of distribution is 1.3 µm and mean diameter is 1.56 µm (see Fig. 1, curve 4). Peak diameter value is 0.75 µm and 69 %.

Further increase of specific treatment energy to 27 MJ/kg doesn't lead to any significant dispersity changes if compared to treatment with $W_s$=18 MJ/kg (see Fig. 1, curve 5).

It is found out that HVED treatment of 80 % Ti + 20 % Fe powder mixture impacts not only the dispersity, but also the shape of particles. Despite the decrease of dispersion dynamics, increase of specific treatment energy leads to an increase of spherical and roundish particles quantity. So, for initial powder content of spherical particles was 15.5 %, content of roundish particles was 61.5 %, content of angular particles was 22.5 % and there was insignificant quantity of rod shape, and after HVED treatment with the increase of specific treatment energy from 9 to 18 MJ/kg content of spherical particles increases from 35 to 46 % due to decrease of roundish (from 56.5 % to 50 %), angular (from 8.5 to 4 %) and rod shape particles content. It is also worth noting that most fine particles after HVED treatment have the spherical shape.

X-ray diffractograms, obtained during study of powders (see Fig. 2) indicate that HVED treatment of powder mixtures leads to synthesis and increase of contents of Titanium carbide as specific treatment energy increases due to interaction between powder mixture components and synthesized nanocarbon.

In case of treatment with minimal considered specific treatment energy ($W_s$=4.5 MJ/kg), presence of free Carbon, which haven't yet participated in carbidization reactions, is observed (see Fig. 2, b). In case of treatment with the maximal considered specific treatment energy ($W_s$=27 MJ/kg), decomposition of Titanium carbide inside discharge plasma with formation of Titanium and Carbon is observed (see Fig. 2, e).



*a*

*b* *c)*

*d)* *e)*

***Fig. 2*** *X-ray diffractograms of 80 % Ti + 20 % Fe powder mixture*
*a – before HVED treatment; b – after HVED treatment with specific energy of 4.5 MJ/kg; c – after HVED treatment with specific energy of 9 MJ/kg; d – after HVED treatment with specific energy of 18 MJ/kg; e – after HVED treatment with specific energy of 27 MJ/kg*

Presence of free Carbon, which haven't participated in carbidization reaction in case of low specific treatment energy (4.5 MJ/kg) or which is formed as a result of Titanium carbide decomposition in case of excess specific treatment energy (27 MJ/kg) leads to a decrease of powder mixture bulk density $\rho_b$ if compared to initial (see Fig. 3). Values of bulk density of powder mixtures after HVED treatment with medium values of specific treatment energy (9 and 18 MJ/kg) are on the level of value of initial powder mixture bulk density due to simultaneous synthesis of Titanium carbide and increase of particles dispersity.

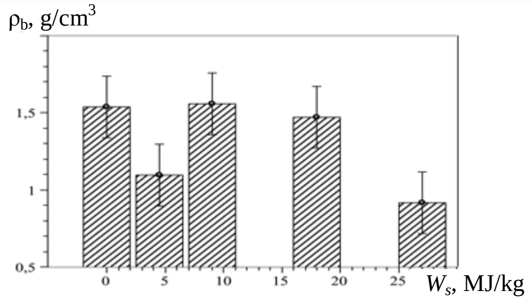


***Fig. 3*** *Bulk density of 80 % Ti + 20 % Fe powder mixture before and after HVED treatment with different specific energy*

Presence of free Carbon in powder mixtures, obtained after HVED treatment with specific energies of 4.5 and 27 MJ/kg also leads to a decrease of hydrostatic density of compacts, consolidated by SPS method from these powder mixtures (see Fig. 4). It is worth noting that all obtained materials have low density (~ 4.8 g/cm$^3$) if compared to conventional HM according to ISO 513–75 of Tungsten (from 13.4 to 15.3 g/cm$^3$), Titanium-Tungsten (from 9.5 to 13.1 g/cm$^3$) and Titanium-Tantalum-Tungsten (from 12 to 13.8 g/cm$^3$) groups.

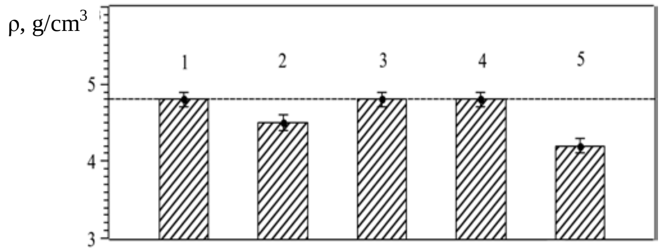


***Fig. 4*** *Density of sintered TLHM*
*1 – sintered from initial powder mixture; 2 – sintered from powder mixture after HVED treatment with specific energy of 4.5 MJ/kg;3 – sintered from powder mixture after HVED treatment with specific energy of 9 MJ/kg; 4 – sintered from powder mixture after HVED treatment with specific energy of 18 MJ/kg; 5 – sintered from powder mixture after HVED treatment with specific energy of 27 MJ/kg*

Mean value of hardness of specimen, consolidated from initial powder mixture, which was not treated by HVED, was 74 HRA. Mean values of hardness of specimens, consolidated from powder mixtures, obtained by HVED preparation with the values of specific treatment energy of 4.5, 9 and 18 MJ/kg, were 82, 83.5 and 84 HRA respectively (see Fig. 5).

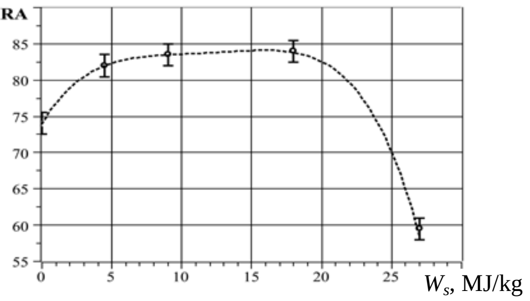


***Fig. 5*** *Hardness of sintered TLHM*

According to GOST 17359–82 (ГОСТ 17359–82), powder hard metal is such a powder material, based on metal-like hard compounds with metallic matrix, which have hardness higher than 80 HRA. Thus, obtained materials belong to hard metals class. Consolidation of powder mixture, obtained by HVED impact with $W_s$=27 MJ/kg, due to formation of excess Carbon, which is formed during decomposition of Titanium carbide in plasma channels, leads to significant decrease of sintered material hardness to 56.5 HRA.

For specimens, consolidated from initial powder mixture, loss of mass during abrasive wear is 4.2 g on 1 km of way (see Fig. 6). Treatment of powders with specific energy values of 4.5 and 9 MJ/kg leads to an increase of abrasive wear resistance of materials, consolidated from such powder mixtures – $m_w$ = 3,1 g/km. Increase of specific treatment energy to 18 MJ/kg leads to further decrease of mass loss of compact to 1.5 g/km. Further increase of specific treatment energy to 27 MJ/kg leads to sharp decrease of wear resistance of material, consolidated from such powder mixture, to $m_w$ = 6 g/km.

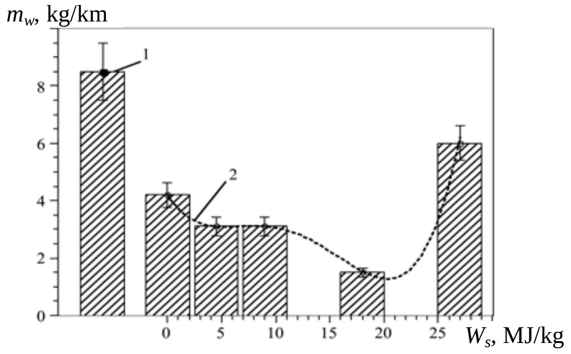


***Fig. 6*** *Loss of mass during abrasive wear*
*1 – VK8 (ВК8) brand hard metal; 2 – obtained TLHM*

Studies of VK8 (ВК8) brand hard metal specimen showed that a significant abrasive wear is observed for this industrial hard metal – loss of mass was 8.5 g for 1 km of way. It is clear that conditions of studies with the use of steel counter-body are different from those used in present work (diamond circle is counter-body), where phenomena of “avulsion” of carbide hardening particles from metal matrix. In this conditions obtained specimens of Titanium carbide hard metal are superior to industrial hard metals by their wear-resistance.

Since thermal conductivity is one of the important characteristics of HM, studies of thermal conductivity of “organic glass – hard metal” system for obtained Titanium carbide hard metals as well as for specimen of industrial VK8 (ВК8) hard metal were performed. Results of these studies indicate that thermal conductivity of obtained hard metals decreases as specific treatment energy of initial powder mixture increases up to 18 MJ/kg (see Fig. 7) due to increase of Titanium carbide content (which has lover thermal conductivity than Titanium). But in case of treatment of initial powder mixture with specific energy of 27 MJ/kg, thermal conductivity of obtained hard metal sharply increases due to presence of free Carbon in compact.

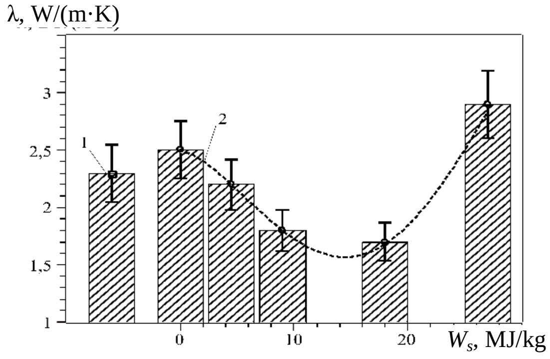


***Fig. 7*** *Thermal conductivity*
*1 – VK8 (ВК8) brand hard metal; 2 – obtained TLHM*

Values of thermal conductivity of obtained Titanium carbide hard metals and industrial VK8 (ВК8) hard metal are close enough (compare Fig. 7, columns 1 and 2). Tungsten carbide has higher thermal conductivity than Titanium carbide which impacts the properties of hard metals that contain them.

Studies of consolidated materials dynamic ultimate tensile strength (see Fig. 8) have shown that for the specimen consolidated from powder mixture treated with specific energy of 4.5 MJ/kg, at strain rate of ~ 800 $s^{-1}$, value of dynamic ultimate tensile strength was ~ 12050 MPa and energy of strain in the moment of destruction beginning was 50 MJ/$m^3$ (see Fig. 8, a).

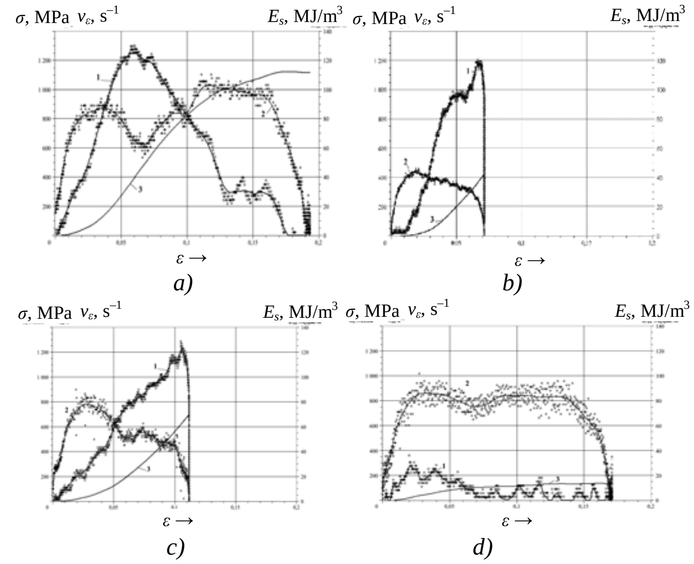


***Fig. 8** Results of sintered TLHM dynamic ultimate tensile strength testing*

*1 – diagram of stress; 2 – diagram of strain rate; 3 – diagram of strain energy*

*a– sintered from powder mixture after HVED treatment with specific energy of 4.5 MJ/kg; b – sintered from powder mixture after HVED treatment with specific energy of 9 MJ/kg; c – sintered from powder mixture after HVED treatment with specific energy of 18 MJ/kg; d – sintered from powder mixture after HVED treatment with specific energy of 27 MJ/kg*

Specimens, consolidated from powder mixture, treated with specific energies of 9 and 18 MJ/kg, at strain rates up to ~ 400 and ~ 800 $s^{-1}$ respectively, have not suffered destruction while maximal strain energy was ~ 40 and ~ 70 MJ/$m^3$ respectively (see Fig. 8, b, c). In case when specimen was consolidated from powder mixture treated with specific energy of 27 MJ/kg, value of dynamic ultimate tensile strength sharply decreases to ~ 300 MPa at strain rate of ~ 800 $s^{-1}$ due to presence of free Carbon in its composition, and strain energy in the moment of destruction beginning is 10 MJ/$m^3$ (see Fig. 8, d).

Considering complex of obtained materials functional properties, it can be concluded that TLHM, consolidated from powder mixture treated by HVED with specific energy in range from 9 to 18 MJ/kg have the optimal properties among considered specimens.

## 4. Conclusion/Заключение

A complex approach to obtainment of Titanium carbide hard metals, which consists of utilization of high density energy flows of HVED for dispersion and activation of particles of powder mixtures of 80 % Ti + 20 % Fe composition, synthesis of carbide phase and subsequent consolidation of obtained powder mixture by high density electric current at electric power of sintering process of 7.5 kJ/s by spark plasma sintering method, is proposed.

Regularities of connection between specific treatment energy of “kerosene – Ti + Fe powders mixture” and changes of dispersity, shape and phase composition of powders and functional properties (hardness, dynamic ultimate tensile strength, wear resistance, thermal conductivity) of TLHM materials, consolidated by SPS, which have high values of strength and wear resistance while their hardness is higher than 82 HRA.

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