ELECTRIC DISCHARGE SYNTHESIS OF TITANIUM CARBIDE

ЭЛЕКТРОРАЗРЯДНЫЙ СИНТЕЗ КАРБИДА ТИТАНА

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Abstract: *Peculiarities of titanium carbide obtainment by high voltage electric discharge synthesis (HVED) are considered in present paper. Mathematical and physical modelling of processes that occur during HVED impact on "Ti powder – hydrocarbon liquid" disperse system is performed. HVED creates thermodynamic conditions for pyrolysis of hydrocarbon liquid with formation of solid-phase carbon and gaseous hydrogen and for synthesis of titanium carbide during reaction of carbidization between titanium and carbon particles. Regularities of connection between HVED parameters and changes of dispersity and intensity of titanium carbide formation*
***KEYWORDS**: HIGH VOLTAGE ELECTRIC DISCHARGE, PLASMA, CARBIDIZATION, POWDERS, TITANIUM*

1. Introduction

Scientific interest to titanium carbide and to development of less expensive methods of its production in particular is connected with a set of unique properties that this material has. First of all, it is a high melting point and hardness, which contributed to fast development of industrial production of tungsten-free hard alloys based on titanium carbide. In its turn relatively high heat resistance and high temperature strength caused the development of methods of tools and constructional products coating with titanium carbide. It is worth noting that recently titanium carbide is increasingly used as an abrasive material [1].

Method of high voltage electric discharge treatment of titanium powder in hydrocarbon liquid [2, 3] is one of the most prospective electric discharge technologies of submicro- and nanosized TiC powders obtainment. Particular attention should be paid to multifactor impact during cyclical HVED treatment of elementary titanium powders which includes thermal impact of low-temperature plasma of discharge channel and electromagnetic and hydrodynamic impact on treated medium. Thermal impact of discharge channel plasma leads to pyrolysis of hydrocarbon liquid with formation of solid-phase carbon and gaseous hydrogen. Synthesized carbon nanoparticles can enter reaction of carbidization with Ti powder particles, with their surface layers in particular, including fresh-formed during impact destruction of Ti 3D-structures.

As the prospect of the use of HVED treatment of titanium powder in hydrocarbon liquid in order to disperse and activate powder as well as to synthesize titanium carbide, has been proven in papers [2,3], it is important to determine the factors which have the most impact on carbidization process and to define the dependences of dispersity and phase composition on impact parameters.

Because of this, *the goal* of present is to find the regularities of dependence of dispersity and intensity of titanium carbide formation on HVED parameters.

2. Preconditions and means for resolving the problem

2.1. Thermodynamic analysis of "Ti powder – hydrocarbon liquid" system under HVED impact

It is known that during HVED temperature of plasma in discharge channel can reach up to ~ $4 \cdot 10^4$ K and pressure - up to ~ 1 GPa [4]. In order to evaluate processes while taking into account processes of possible reactions and formation of their final products, thermodynamic analysis of equilibrium processes, which is used in theory of metallurgy and welding for forecasting of the course of reactions, was used. Usage of this method allows assumption that, despite short duration of the process, high temperature of metal heating and large specific area of contact ensure thermodynamic equilibrium [5]. Moreover, in paper [6] it is stressed that during electric discharge treatment thermodynamic processes can be considered adiabatic because of pulses short duration. Thermodynamic calculations are based on values of enthalpy *H*, entropy *S*, heat capacity C_p and Gibbs energy *G* for chemical compounds. The nature of Gibbs energy change gives an indication of the fundamental possibility of considered process. Methods of thermodynamic analysis are considered in [7] in details.

For all components of kerosene model analog for reactions of decomposition to carbon and hydrogen evaluated ΔG value is negative for decomposition of both liquid and gaseous phase. Generally, HVED impact on hydrocarbon medium by plasma channel allows obtainment of carbon in different phase states.

The inner temperature of the plasma in discharge channel which reaches up to ~ $4 \cdot 10^4$ K is only slightly dependent on value of energy and time of its release [4]. Energy, released inside discharge channel, is mainly spent on heating of substance inside discharge channel and on the work of channel expansion on surrounding liquid. It turns out that energy, spent on heating of substance, is concentrated in relatively equally heated area of channel, while energy stored in thin transition layer between plasma and liquid is relatively small. Its thickness δ can be evaluated as $\delta \sim 2\sqrt{\chi \cdot \tau}$, where χ – coefficient of thermal conductivity, m^2/s; τ – duration of first semiperiod of discharge, s [4].

For discharges in kerosene thickness of transient layer is microns (for example, for temperature of 900 K and pressure of 4 MPa $\chi = 1{,}7 \cdot 10^{-7}$ m^2/s, at t=5 μs thickness of layer is $\delta \approx 1{,}85$ μm), which is enough for correct evaluation of processes occurring in this area. Therefore, to achieve efficient carbidization, it is necessary to create conditions at which plasma channels will be distributed through all volume of reactor.

In considered system, the most probable reaction is formation of titanium carbide TiC (see Fig. 1) in wide temperature range.

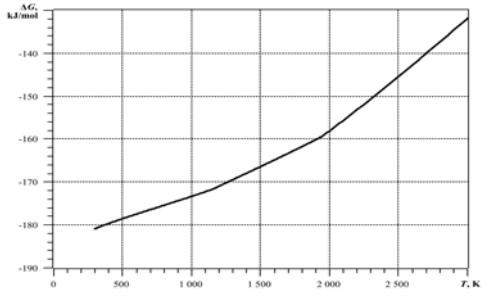


***Fig. 1** Dependence of Gibbs energy change of Ti + C → TiC reaction on temperature*

2.2. Methods of research

A flat, transparent discharge chamber was manufactured for physical modelling of electric discharge processes that occur in Ti powder layer, which allowed photo registration of discharges in layer of powder [9, 10]. Ti of d_m=100 μm fraction in kerosene was an object of study. Distance between chamber walls was D=5 mm. A tip – plane electrode system was used for modelling. A reflex photo camera with shutter speed set in range from 2 up to 3 s was used for photography.

Experimental studies of the impact of HVED parameters on regularities of change of dispersity and phase composition of Ti powder were conducted on experimental stand, described in details in work [11], with variation of specific treatment energy in range from 10 up to 40 MJ/kg. Studies of hydrodynamic characteristics of HVED were performed in discharge chamber by waveguide pressure sensor (WPS) [12,13].

Optic and electron microscopes BIOLAM-I (БИОЛАМ-И) and REMMA-102 (РЭММА-102) were used for evaluation of HVED impact on powders particles size. Phase analysis was performed on D8 Bruker ADVANCE X-ray diffractometer (CuKα) and analog-to-digital converter. Analysis of obtained X-ray diffraction patterns was performed in QualX software with PDF-2 and POW_COD bases [14].

2.3. Physical modelling of distribution of plasma formations during HVED in kerosene – Ti powder" system

Studies have shown that plasma formation appearance is observed during treatment of "titanium powder – hydrocarbon liquid" disperse system (see Fig. 2). In the beginning of studies plasma formations were observed in areas adjacent to anode and cathode (see Fig. 2, a, b) which lead to increase of gap between anode and powder layer. On the photo of 10^{th} pulse it worth noting that local plasma formations begin appearing between particles in powder layer and that diameter of plasma formation in near-anode area increases, which indicates the increase of fraction of energy released in region between anode and powder layer. Further increase of fraction of energy released in this region leads to increase of hydrodynamic impact of gas-vapor cavity on the medium, mixing of powder and formation of Ti particles suspension in kerosene (see Fig. 2, c). Plasma formations in central part of chamber, united in channels, slowly displace powder to chamber corners, decreasing concentration of solid phase in central region which leads to increase of interelectrode gap resistance value (see Fig. 2, c, d).

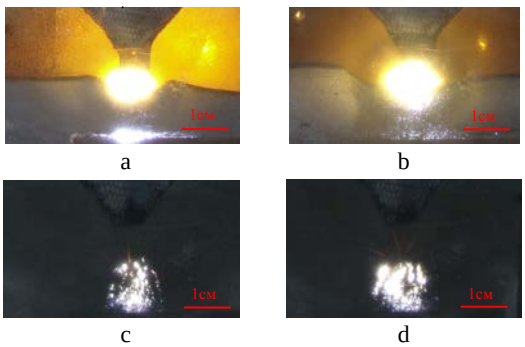


Fig. 2 *Integral photos of discharge in "Ti powder – kerosene" disperse system with single discharge energy W_1 = 90 J and initial dispersity d_m = 100 μm after 5^{th} (a), 10^{th} (b), 50^{th} (c) u 100^{th} (d) pulses*

Fig. 2, c, d clearly shows the multifactorness of electric discharge impact on disperse powder – thermal impact of low-temperature plasma of discharge channel and hydrodynamic impact. Integral shots of discharges in disperse system show, that changes of solid phase concentration in discharge gap leads to significant change of plasma formations distribution in volume of discharge camber. Decrease of solid phase concentration in interelectrode gap leads to increase of hydrodynamic impact while electroerosion destruction of particles – removal of liquid-phase metal from treated particles surface under the impact of electrodynamic forces – weakens. It is also worth noting that decrease of concentration of solid phase in interelectrode gap leads to unnecessary intensification of carbon formation processes.

Therefore, to choose regimes of powders treatment it is necessary to find connection between pressure amplitude and concentration of solid phase and discharge circuit parameters.

2.4. Study of hydrodynamic characteristics of HVED in "kerosene – Ti powder" system

Analysis of results if experimental study of pressure amplitude during HVED in kerosene (see Fig. 3) indicates the tendency of pressure amplitude increase from ~10 to ~25 MPa as a result of increasing capacitors capacity from 0.4 to 1.6 μF.

In case of variation of capacitors capacity in range from 0.4 to 1.6 μF during HVED in kerosene with addition of Ti powder (S:L rate 1/18) values of pressure amplitude (see Fig. 3, curve 3) decrease ~1.8 times in average if compared to HVED in kerosene in similar regimes (see Fig. 3, curve 1).Experimental values of pressure amplitude in regime with C=1.6 μF during HVED in kerosene and in kerosene with addition of Ti powder (S:L rate 1/18) are ~26 and ~13 MPa respectively (13 MPa difference) while the standard deviations of the respective data sets are 8.84 and 2.76 MPa respectively.

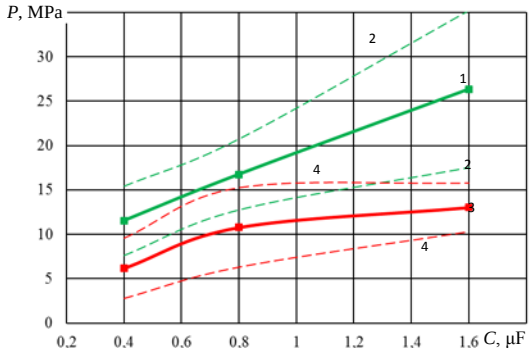


Fig. 3 *Pressure amplitude during HVED with the use of kerosene as continuous medium*
1 – pressure amplitude during HVED in kerosene; 2 – standard deviation of data set of HVED in kerosene; 3 – pressure amplitude during HVED in kerosene with addition of Ti powder (S:L rate 1/18); 4 – standard deviation of data set of HVED in kerosene with addition of Ti powder (S:L rate 1/18)

During HVED in kerosene in regimes with C=0.4 and 0.8 μF pressure wave front velocity matches speed of sound in kerosene (v = 1330 m/s) within margin of error. Increase of capacitors capacitance leads to increase of average pressure wave front velocity to 1363 m/s which indicates formation of shock waves.

Addition of Ti powder in kerosene (S:L rate 1/18) leads to decrease of pressure wave front velocity in regime with C=0.4 μF to 1270 m/s (see Fig. 4, curve 3), which is less than speed of sound in kerosene. Increase of capacitors capacitance to 1.6 μF doesn't lead to significant changes of experimentally registered pressure wave front velocity. Yet, as it was mentioned earlier (see Fig. 3), amplitude of pressure on WPS in this regimes rises from 10 to 13 MPa, which confirms the assumption of interaction between pressure wave front and particles of disperse phase suspended in continuous medium.

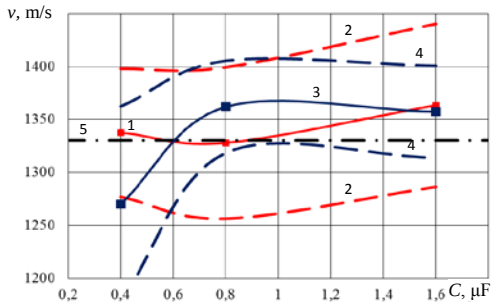


Fig. 4 *Velocity of pressure wave front during HVED with the use of kerosene as continuous medium*
1 – pressure wave front velocity during HVED in kerosene;
2 – standard deviation of data set of HVED in kerosene;
3 – pressure wave front velocity during HVED in kerosene; with addition of Ti powder (S:L rate 1/18); 4 – standard deviation of data set of HVED in kerosene with addition of Ti powder (S:L rate 1/18); 5 – speed of sound in kerosene

2.5. *Study of changes in phase composition and dispersity*

Dynamics of processes of carbidization of Ti powders was studied by X-ray diffraction phase analysis (see Fig. 5) of powders while increasing specific treatment energy in range from 2 up to 20 MJ/kg.

It was found out that treatment with specific energy W_{sp}=2 MJ/kg leads to synthesis of titanium carbide phase (see Fig. 5, b) and its content is ~11 %. Increase of specific HVED treatment energy to W_{sp}=10 MJ/kg leads to significant increase of quantity and intensity of titanium carbide TiC peaks (see Fig. 5, c) and its content rises to 40 %. Further increase of specific energy to W_{sp}=20 MJ/kg leads to increase of titanium carbide content to ~71 % and increase of TiC peaks intensity (see Fig. 5, d).

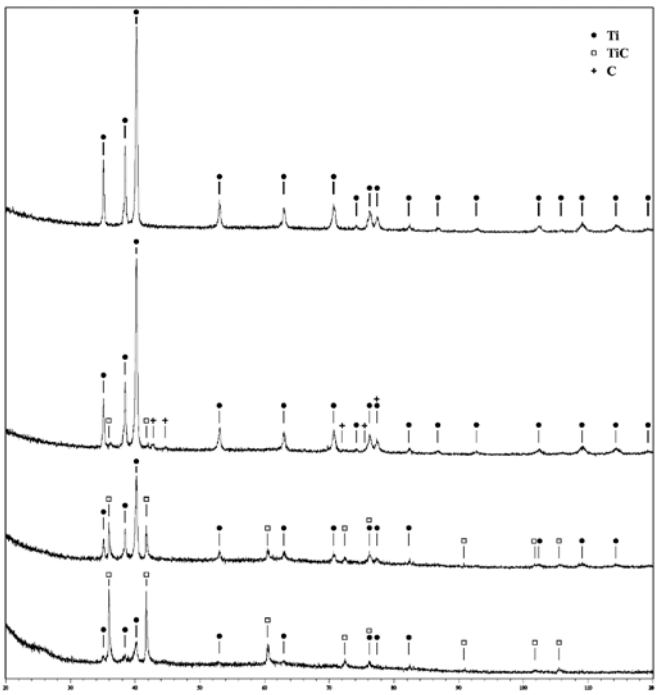


Fig. 5 *X-ray diffractograms of Ti powder, initial (a) and after HVED treatment with specific energy W_{sp} 2(b), 10 (c) and 20 MJ/kg (d)*

Dependence of titanium carbide quantity change (calculated with X-ray diffractograms) on specific treatment energy (see Fig. 6) can be evaluated by power function:

$$C_{\mathrm{Ti}} = 6.335 \cdot W_{sp}^{\ 0.805} \qquad (1)$$

where C_{Ti} – is a quantity of titanium carbide, %; W_{sp} – specific treatment energy, MJ/kg. This function allows calculation of specific treatment energy necessary for carbidization of titanium powder.

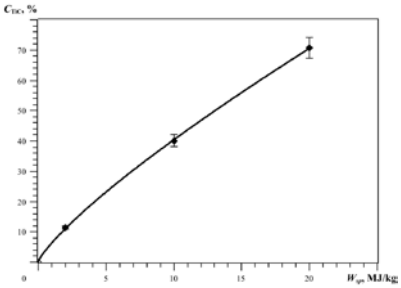


Fig. 6 *Dependence of quantity of synthesized titanium carbide on specific treatment energy*

It is clear that carbidization processes are accompanied by powders dispersion and activation. Results of studied have shown that the most intense 12 times grinding of treated powder (see Fig. 7) during HVED occurs after treatment with specific energy of 10 MJ/kg, maximal peak of particles sizes of 37 % lies in range of 1.3μm (see Fig. 8), which, as was mentioned earlier, contributes to carbidization and formation of ~40 % TiC. As a result, dispersed and activated titanium powder actively reacts with synthesized nanocarbon particles, forming titanium carbide.

Further increase of specific energy to 30 MJ/kg dispersion intensity decreases, but grinding continues to size of 0.3μm and is 40 %. Further increase of specific energy to 40 MJ/kg impacts value of mean diameter insignificantly, but peak of particles size distribution moves to point of 0.3 μm and is 47 % (see Fig. 9)

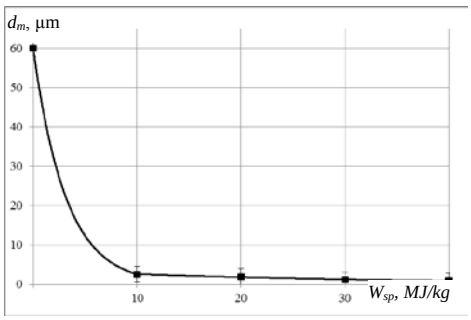


Fig. 7 *Dependence of Ti powder mean diameter after HVED treatment on specific treatment energy*

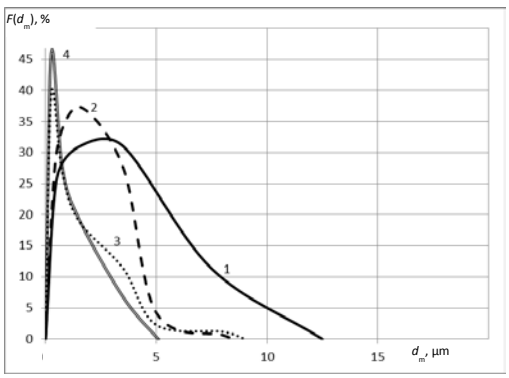
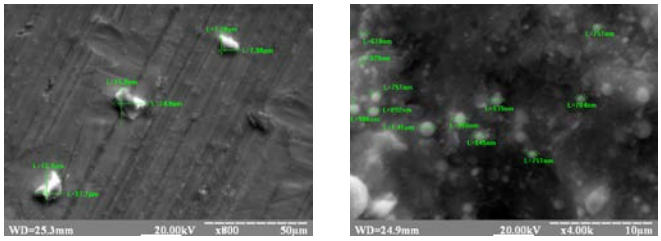


Fig. 8 *Distribution of percent content $F(d_m)$ of Ti powder particles by values of mean diameter d_m after HVED treatment with specific energy W_{sp} 10 (1), 20 (2), 30 (3) and 40 MJ/kg (4)*



a b

Fig. 9 *Microelectronic photos of Ti powder, initial, magnification ×800 (a) and after treatment with W_{sp}=40 MJ/kg, magnification ×4000 (b)*

3. *Conclusion*

Conditions, necessary for efficient electric discharge synthesis of titanium carbide, are theoretically justified and experimentally confirmed.

Conducted studies allowed finding regularities of connection between kinetics of processes of dispersion, activation and synthesis of titanium carbide and HVED treatment parameters

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4. Literature

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