PLASMA TECHNOLOGIES FOR OBTAINMENT OF COMPOSITE MATERIALS DISPERSION HARDENED BY NANOSTRUCTURED PARTICLES

ПЛАЗМЕННЫЕ ТЕХНОЛОГИИ ПОЛУЧЕНИЯ МНОГОФУНКЦИОНАЛЬНЫХ ДИСПЕРСНОУПРОЧНЕННЫХ НАНОСТРУКТУРИРОВАННЫМИ ЧАСТИЦАМИ КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ

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Abstract: Prospects for creation of plasma electric discharge technology for production of dispersion-hardened by nanoparticles composite materials are considered. Physical modelling of plasma formations distribution in discharge camera is performed. The regularities of the electric discharge processing parameters influence on dispersity, phase composition and electrical resistivity of obtained powders are studied. The regime for spark plasma sintering of processes powders is theoretically and experimentally justified.
***Keywords**: PLASMA TECHNOLOGY, ELECTRIC DISCHARGE, SPARK PLASMA SINTERING, POWDERS, CARBIDE-STEEL*

1. Introduction

The expectations of the industry to the hardness and wear resistance of structural and tool materials increases, so obtainment of multifunctional materials by powder metallurgy is promising [1]. Properties of consolidated powder material depends both on the properties of the initial blend and on the mode of its sintering. In turn, the properties of the blend depends largely on the method of its preparation. Conventional mechanical milling is quite energy consuming and leads to the appearance of inclusions, which could affect the properties of the consolidated material [2]. It is known that conventional consolidation methods lead to grain growth due to prolonged heating.

A new approach in developed plasma technologies consists in the fact that dispersion-hardening additives (in particular, TiC and TiB_2) are not introduced mechanically to the powder mixture as an additional component in the blending of powders, as in the conventional methods, but instead are formed during electric discharge (ED) processing as a result of the reaction of synthesis under the influence of microplasma discharges. A distinct feature of new approach for creating dispersion-hardening additives is the implementation of a cyclic pulse (a few microseconds), substantially non-oxidizing ED in the disperse system "hydrocarbon liquid - powder". Due to the pyrolysis of hydrocarbon liquids by discharge plasma channel, nanocarbon of various allotropic forms (depending on the composition of the fluid) is synthesized. Intense thermal (plasma) and mechanical (shock wave) impact on the initial powders and mixtures thereof is accompanied by an increase in the number of defects in the crystal structure that promotes activation and dispersion of particles material. Also, due to exposure to low temperature plasma melting or evaporating of particles may occur, which leads to changes in their properties during rapid cooling in liquid. The prospect of using ES technology is associated with the possibility of obtaining a uniformly distributed micro-and nano-sized particles with a high level of free energy in the composition of the powder blend and, consequently, with an increased ability to intensively react with nanocarbon particles to create a strengthening phases.

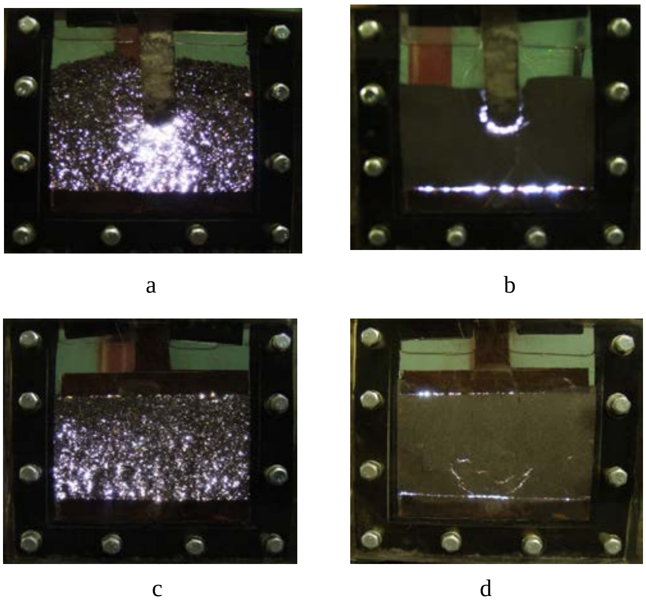
Preservation of high dispersion of the products material grains is carried out through the use of spark plasma sintering (SPS). During SPS, which consists in passing the pulsed current (superposition of AC and DC) through the powder while the mechanical seal, plasma formation in the gas phase that fills the gaps between the particles arouses. This contributes to the rapid heating and (under external pressure) intensive compaction to almost nonporous state that would greatly ensure the safety of the ultrafine structure and makes possible obtaining high-density powder composites with improved physical and mechanical properties [3].

The aim of present work is consideration of a holistic approach to the technology of obtaining multifunctional, dispersion-hardened by nanostructured particles composite materials using a set of plasma processing technologies containing steps from the production of powder blend to production a finished product with improved functional properties.

2. Modelling of electric discharge processes in a layer of Ti powder in kerosene

Effective management of the processes of plasma ED preparation of powders requires knowledge about the influence of the configuration of the electric field (studies have been performed with the systems of the point-plane or plane-plane) and the dispersion of the treated powder patterns on distribution of plasma formations and nature of the process of high-voltage electrical discharge. Therefore, physical modeling of electric discharge processes occurring in a layer of Ti powder in kerosene was performed. The use of flat, transparent discharge chamber, allowed to photograph discharges in powder thicker. During the investigations it was found that the use of the electrode system (ES) point-plane, as compared with the case of applying ES plane-plane, increases the density of the plasma formations in the central area of the chamber and as a consequence, increases current density and the proportion of the energy released in that area. Application of plane-plane system allows to achieve greater uniformity of treatment of the powder, but the use of the point-plane in conjunction with the mode of processing, which provides mixing particles of the powder, improves the processing efficiency due to the concentration of energy to the electrode region. It is also found that the influence of the electric field configuration on the distribution of plasma formation is minimized by reducing the average diameter (d_{av}) of the processed powder (see Fig. 1).

Obtained results were used for the design of electric discharge reactors in the development of plasma technologies. The dependence of the distribution of plasma formations in the discharge chamber on the dispersion of the processed product and the configuration of the electric field showed the possibility for development of new technological methods for powders ED processing oriented on changing the morphometric characteristics of the solid phase and its phase composition.



a – d_{av} =1mm, ES point-plane; b – d_{av} =0,1mm, ES point-plane; c – d_{av} =1mm, ES plane-plane; г – d_{av} =0,1mm, ES plane-plane

Figure 1 *– Integral images of discharges in the disperse system "titanium powder in kerosene."*

3. Impact of ED processing on dispersity and phase composition of obtained powder blend

Results of physical and theoretical modeling of ED processes in the disperse system "metal powder - kerosene", presented in Section 2 and papers [4, 5], helped to create an experimental stand and to set processing modes, providing high dispersion of the powder and the appearance of a dispersion-hardening phases [5].

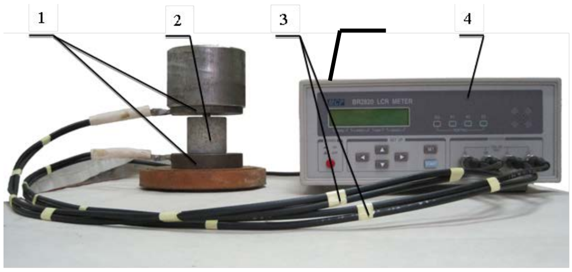
Regularities of impact of current rise rate, pressure in discharge channel, integral energy and processing time onto regularities of morphometric characteristics change and dispersion kinetics of powder mixtures 75 % Fe + 20 % Ti + 5 % B_4C (mass portions) and 80 % Fe+20 % Ti (mass portions) as well as of Fe and Ti powders in kerosene were experimentally found out. It is established that ED treatment with current rise rate *di/dt* ~ 28 GA/s and integral energy W_Σ=4 MJ allows to obtain highly disperse (35 % of particles has sizes from 0,05 to 1 μm) homogenous blend for carbide steels – system of iron-carbon alloy – carbide (diboride) of titanium.

Phase composition of powder mixture 75 % Fe + 20 % Ti + 5 % B_4C (mass portions) after ED treatment changes in every one of chosen and theoretically justified treatment regimes. Achievement of current rise rate no less, then ~ 17 GA/s is a condition for formation of phases like TiC, FeB, Fe_2Ti and $Fe_3(B_{0,7}C_{0,3})$. The regularities of communication of titanium powder carbidization (up to 98 %) with an increase of current density j_k in the discharge channel from 0,08 to 0,56 kA/mm^2 are found out. ED treatment opens a way for controlling homogeneity of synthesized titanium carbide by variation of energetic parameters and allows obtaining powder blend, saturated with nanostructured dispersion-hardening carbides and borides particles.

4. Changes of powder blend electrical resistivity as a result of ED processing

When using electric current consolidation methods electrical resistance of the powder composition plays an important role: high resistance impedes the flow of current, resulting in uneven heating of the sample and disruption of its integrity. Electrical resistance of metal powders is associated with the composition, size and shape of the powder particles. Thus, a large amount of coarse particles of spherical or fragmental shape reduces contact area and increases the value of electric resistance. It is possible to reduce electrical resistance by varying the fineness and shape of the powder particles, and removing a surface oxide film. As shown in Section 3, ED treatment leads to a refinement of the particles, changing the shape and phase composition of the powder, which should affect the change in electrical resistance of the blend.

Studies of electrical resistance change of powder compositions 75% Fe+25% Ti and 75%Fe+20%Ti+5% B_4C, treated by ED in kerosene with constant total processing energy 1 MJ and variation of single discharge stored energy in the range from 0.25 to 1 kJ (amount of energy stored in the capacitive storage and released to the work environment at one discharge of a series) were performed. Experimental stand (see Fig. 2) was assembled to determine the electrical resistance. Powder was filled in a dielectric cell (Fig. 2, position 2), which was then put in the press (not showed on Figure), and then cyclic loading of samples was performed. The number of cycles was at least 3, the pressure load of each series of cycles ranged from 0.6 to 60 MPa.



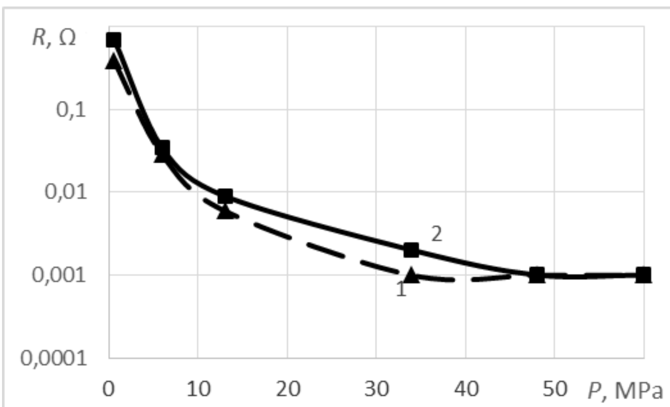
1 - punch - contacts; 2 – dielectrical cell; 3 – commutation cables; 4 - MCP "BR 2820" LCR METER; 5 – load, providing pressure of 0,6 MPa

Figure 2 *– Stand for the resistance of the powders determination*

It is found out that composition of studied mixture has significant impact on electrical resistance: presence of semiconductive B_4C (5 %) in the composition of 75 % Fe + 20 % Ti mixture leads to the increase of electrical resistivity from ~ 120 up to ~ 200 kΩ.

ED treatment of powder mixtures of 75 % Fe + 25 % Ti and 75 % Fe + 20% Ti + 5% B_4C compositions leads to decrease of electrical resistance from ~ 120 and ~ 200 kΩ to ~ 1,5 and ~ 400 Ω with W_1=0,25 kJ and to ~ 0,4 and ~ 0,7 mΩ with W_1=1 kJ respectively to composition.

Increase of mechanical pressure from 0,6 up to 60 MPa leads to decrease of electrical resistance *R* of studied powders, but it is still affected by presence of boron carbide. However ED treatment of the mixtures with W_1 = 1 kJ leads to the fact that when a pressure is greater than 40 MPa, the composition of the initial mixture does not affect the electrical resistivity (see Fig. 3).



1 – 75% Fe+25% Ti; 2 – 75%Fe+20%Ti+5% B_4C;

Figure 3 *– Dependence of the electrical resistivity of powder mixtures of different initial composition after ED treatment with W_1 = 1 kJ on the prepressing pressure*

Analysis of data obtained by measuring the electric resistance of the powder mixtures allows to select the optimum characteristics of consolidation by electric current depending on the initial pressure. Furthermore, the obtained dependencies of powder electrical resistance on its particle size and phase compositions have allowed to establish the methodology of express analysis of resulting powder blend quality by monitoring its electrical resistance without direct study of dispersion and phase composition.

5. Technological methods of spark plasma sintering of powder blend, obtained by plasma ED technology of powders preparation

To preserve fine-grained structure of the material during the sintering methods of consolidating the concentrated streams of energy are used. These methods are characterized by high heating rates and less time of holding at the maximum temperature than when using conventional methods of sintering. Spark plasma sintering (SPS) is one of such methods [3].

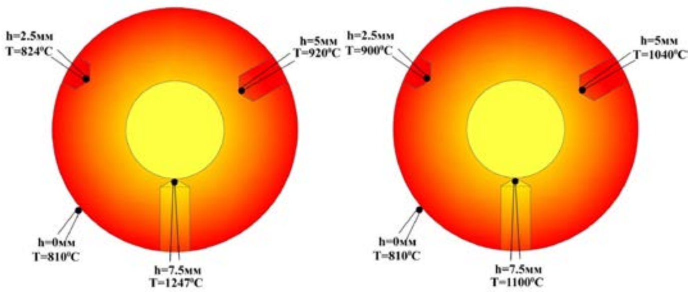
Experimental SPS complex "Gefest-10" [6] has been developed in IPPT NASU. This complex is based on the direct passage of output current with an amplitude value of 1 kA (superposition of DC and high frequency, up to 10 kHz AC) through powder composition. Direct current heats evenly all section of the briquette, but due to the heat sink peripheral areas are cooled. The alternating current due to skin effect is partly displaced to the surface section of the sample and preferably carries out heating of the peripheral portion. This compensates for the effect of the heat sink and aligns temperature conditions over the section of specimen.

"Gefest-10" experimental complex consists of current source, manual hydraulic press PRG -1, vacuum chamber, vacuum pump 2NVR-5DM and control systems. Current source - spark-plasma sintering generator, consists of high-frequency power rectifier - transformer module, a high-frequency inverter with an air cooling system, the transistor driver and the control system. 'Gefest-10" contains RS-485 digital Interface for displaying controlled parameters of temperature in the sintering zone, the current through the sintered sample and voltage across sintering chamber current buses on the PC.

Studies were performed using blend, prepared by plasma ED method (see Sections 3, 4). Power of heat flow was calculated using experimentally measured values of electrical resistivity of blank during sintering[7]. It allowed theoretical evaluation of thermal field distribution in matrix basing on Fourier law (see Fig. 4, a).

Experimental verification of the theoretical evaluation of distribution of the thermal field in the matrix was performed by examining the distribution of the temperature field with thermocouples by drilling during walls of graphite matrix to a depth of 2.5, 5 and 7.5 mm from the surface (see Fig. 4, b). Matrix made of MPG-6 graphite with wall thickness of 7.5 mm was used, the weight of obtained samples was 3 grams, height 7 – mm, diameter - 10 mm.

Theoretical evalution of the thermal field distribution and experimental studies of sintering system Fe-Ti-BC blend showed the existence of low-melting eutectics, that facilitates high-density material, when the temperature on the surface of the matrix T = 810 ° C (the temperature of sample T = 1100 ° C). Blend compaction kinetics was studied to determine optimal heating ratio when entering the sintering regime. Ashby power creep model was chosen as a model of deformation [8].



a b

a – theoretical distribution of thermal field; б – experimental distribution of thermal field

Figure 4 *– The stationary distribution of the temperature field through the thickness of a single layer of the cylindrical wall of the graphite matrix with the theoretical calculation of control points*

It is found that at a heating rate of 100 °C/min. (1,65 °C/s) sample, which was released on the exposure mode, has a total porosity of about 10%, which is reduced to 1-2% during exposure (exposure time – 120 s). Further increase of heating rate leads to increase of porosity, and decrease of heating rate increases the possibility of structure grain growth.

Accuracy of presented methodology was tested on the example of the SPS of blend, batch obtained by ED treatment of powders mixture 75% Fe-20% Ti-5% B_4C. Taking into account performed experimental and theoretical studies such SPS parameters were selected: sintering pressure P=60 MPa, heating rate when entering sintering mode – 100 °C/min. (1,65 °C/s), holding temperature T=810 °C, holding time τ=120 s.

Flexural strength of obtained metal matrix composites amounted up to 1350 MPa, hardness - 68 HRC, frictional wear resistance paired with diamond wheel - 28 mg / km. For comparison - wear resistance of high-speed steel P6M5 under these conditions is 40 mg / km.

Conclusions

1. The holistic approach to the technology of obtaining multifunctional, dispersion-hardened by nanostructured particles composite materials using a set of plasma processing technologies containing steps from the production of powder blend by ED preparation of powders to production a finished product with improved functional properties by SPS was developed.

2. Established dependence of nature of plasma formations distribution in the discharge chamber on the dispersion of the processed product and the configuration of the electric field led to the development of new technological methods of ED powders treatment targeting both the change in morphometric characteristics of the solid phase and its phase composition

3. The parameters of ED processing for obtaining fine (35% has a size of 0,05 to 1 μm), uniform blend for carbide steels and for carbidization of titanium powder (up to 98%), are established which allows to obtain a powder blend, saturated with dispersion-hardening nanostructured particles of carbides and borides.

4. The methodology of express analysis of resulting powder blend quality by monitoring its electrical resistance without direct study of dispersion and phase composition is developed.

5. Technological methods for spark plasma sintering of powder blend, obtained be plasma ED technology of powders preparation, are developed.

4. Possibility for obtaining material with almost theoretical density, hardness up to 68 HRC, flexural strength of 1350 MPa and wear resistance higher, than of high-speed steel P6M5, is shown.

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