PULSED DISCHARGE TECHNOLOGIES OF PROCESSING AND OBTAINMENT OF NEW MATERIALS (Review)

РАЗРЯДНОИМПУЛЬСНЫЕ ТЕХНОЛОГИИ ОБРАБОТКИ И ПОЛУЧЕНИЯ НОВЫХ МАТЕРИАЛОВ
(Обзор)

Prof., Doctor of Science Sizonenko O., Prof., Doctor of Science Vovchenko A.
Ukraine, Mykolaiv, Institute of Pulse Processes and Technologies of NAS of Ukraine
E-mail: sizonenko43@rambler.ru

Abstract: *Review of pulses discharge technologies (PDT), in which pulses electric discharge in liquid is utilized, is given. PDT of processing and obtainment of new materials allows to impact both changes of geometrical size and the structure of objects in order to give it certain mechanical and physical properties. They are used in oil production, instrumentation, mechanical engineering, metallurgy, chemical industry, mining complex, and other.*

KEY WORDS*: ELECTRIC DISCHARGE IN LIQUID, SYNTHESIS, NANOMATERIALS, METAL-MATRIX COMPOSITES, SPARK PLASMA SINTERING*

1.Introduction

All variety of PDT using intense pulsed electric discharge (ED) in the liquid is reduced to the processes taking place at the explosive transformation of electrical energy into other forms of energy during the 1-100 ms. Therefore, methods of processing materials using electrical discharge in the liquid reasonably are related to a class of pulsed methods. Due to the high energy density (10^4 - 10^5 J/cm^3) in a limited volume of the discharge channel the pressure therein reaches 10^8 - 10^9 Pa and shock extension of the discharge channel is observed. As a result, powerful compression waves, acoustic fields, the complex cavitation (from micro to macroruptures) phenomena, electromagnetic and light radiation are generated in medium. The use of these factors of the ED is the basis of electric discharge methods for processing and obtainment of new materials. Technological equipment for ED treatment, regardless of the specific purpose and an object of processing, has identical block diagram and consists of the following main parts: [1] generator of pulse currents (GPC) with capacitive energy storage, discharge circuit, the discharge-processing unit, integrated control block for GPC and technological cycle.

2. Analysis and discussion

For analysis and discussion PDT, which are the most widely used for the processing and production of new materials, are presented.

2.1 PDT of intensification of filtration processes in porous materials – stimulation of oil wells [2].

The essence of this PDT is that in a borehole filled with liquid, using a high voltage pulse discharge such fators are aroused: electromagnetic and thermal fields; cyclic compressional waves with an amplitude of up to 50 MPa at the fron,; which are transformed into acoustic waves with the spectrum of frequencies from 10 Hz to 10 kHz; powerful hydrostreams (speed at the front of ~ 150 m/s) and volume microcavitation. A distinctive feature of PDT of oil wells stimulation is the ability of selective processing of local area of productive horizon. This PDT is eco-friendly, simple and reliable in operation with minimum energy consumption (power consumption of an electric downhole device no more than 2 kW).

This PDT promotes: the creation of non-additive (synergistic) effect in change (improvement) of the filtration characteristics of porous materials saturated with liquid with deep stratification (productive oil reservoirs), the removal of all types of deposits in the near-wellbore zone, prevention of the subsequent crystal growth of deposits and their sticking to the surface, contributing to the increase of processing effect time; development of existing cracks and the creation of new fracture channels; removal of contaminants from the pores; destruction of structural skeleton of oil inside the pores, enhancing its mobility by filtration (reduced yield stress, shear stress and dynamic viscosity); increase of the reservoir impact coverage by increasing penetrating filtration capacity of reactive compounds.

PDT can be implemented to improve the performance of production and injection wells during underground and major repairs; processing of bottom-hole zones of high strata, waxy crude oils and bitumen; provocation of influx into the well during development; provocation of influx from potentially productive layers of prospecting and exploration wells.

Electric discharge method of synergistic effect creation in improving the filtration properties of porous materials of deep stratification is adapted to porous materials of artificial origin - the regeneration of the filter elements[3].

2.2 PDT of electric hydro pulse processing (EHPP) of liquid and crystalizing metal [4].

The peculiarity of this technology is the fact of incompatibility of the physical parameters of the object (high temperature) and a liquid medium in which the ED can be realized. Therefore, in this PDT an electric discharge generator of elastic vibrations (EDGEV) is applied in the discharge-processing block, wherein the solid barrier (eg, membrane) placed at the boundary between two media, transforms ED in fluid into the elastic vibrations that affect the subject of the treatment (liquid metal) .

The essence of the EHPP method is to generate elastic vibrations by discharge in water filling EDGEV and to transmit these vibrations into the melt through the waveguide-radiator system (waveguide). Different modifications of EDGEV allow to realize electric discharge processes in wide range of electric parameters change: voltage from 1 up to 50 kV; current from 1 up to 30 kA; discharge pulses frequency from 1 up 16 Hz. Currently accumulated experience of EHPP of nonferrous metals and alloys of iron shows some positive effects resulting from treatment: reducing the inhomogeneity of chemical elements distribution; reduction of diffusion-movable oxygen and hydrogen; grinding and removal of nonmetallic inclusions; increase in fracture toughness, impact strength and formability of steels; intensification of the processes of degassing, refining and homogenization of the melt which creates conditions for a more homogeneous crystallization.

EHPP of melt in the ladle by EDGEV waveguide before casting applied to alloys based on Fe and Al increases the crystallization ability of the metal - a key factor in the formation of the solid metal properties. Efficiency of melt EHPP includes: the removal of free hydrogen by at least 30%; reducing the number of nonmetal inclusions by 15%; grinding macro and microstructure; lowering the threshold of cold brittleness at 20 ºC; reduction in variability of the mechanical properties by at least 15% (the casting of shipbuilding and general purpose steel); increase the wear resistance by not less than 50% (high-carbon alloy castings, operating under hydro wear); reduction of magnetic permeability in high-carbon alloys for electrical purposes by 4 – 10%; increase of the tightness of complex configuration aluminum alloys castings at high operating pressures; 10%; reduction of the harmful effects of iron impurities and structural heredity when remelting of secondary aluminum alloys.

2.3 PDT of intensification of materials volumetric deformation [5]

PDT of volumetric deformation of materials include PDT aimed directly at changing the shape of the processed material without significant destruction. Such PDT includes electrohydraulic stamping (EHS), press-fitting of tubes in heat exchangers, as well as electro-treatment of the welds.

EHS is based on realization of ED in working chamber and transmission of pressure, which arouses during discharge channel extension, to the processed blank directly or by die. In this case, the blank takes the desired shape by a special matrix.

he particular feature of the pulse-static deformation is that the energy of the electric discharge is not aimed at creating forces deforming part, but instead at agitation of waves of mechanical stresses and deformations in the material which, together with the static loading stresses cause plastic deformation of the parts. Static constituent of load creates elastic deformation of part, and pulsed constituent transforms it into plastic by means of elastic stresses relaxation. Such method of deformation significantly decreases the energy of pulse load and power consumption of used equipment. The same level of stress relaxation in the material and the amount of plastic deformation can be obtained both by increasing the impact pulse parameters and by achieving high stresses of elastic strain (up to the yield point) at the lower pulsed load.

Pulsed-static deforming creates favorable conditions for the relaxation of residual stresses in a formed or calibrated part.

Major advantages of EHS over conventional press stamping are: punching precision is improved because of the reduction of stresses, especially when processing most hardly-deformed metals; possibility of obtaining solid components of complex shapes in a single passage, whereas in conventional methods such parts require several passages and are performed welded; increase of materials deformation permissible degree; possibility of producing parts that are economically unviable, or impossible to produce by other methods; improved surface quality of stamped parts; greatly simplifies and reduces the cost of tooling, thereby reducing the time of preparation of manufacture.

2.4 PDT of destruction of durable nonmetallic objects consists in using forces from the shock wave generatedbya high voltage discharge in a liquid [6]. As well as in case of explosives use, in destructible object holes are performed, into which water is poured and electrode system is placed. When a high voltage from the GPC is applied to the electrode system, the discharge occurs in the discharge gap. This process is accompanied by extension of discharge channel, rise of pressure that can reach up to 10^9 Pa and formation of shock wave.

Destruction of soils, concrete and reinforced concrete objects occurs by creating cracks occurring in all directions around the hole, with subsequent separation of the solid pieces. Number of cracks, their depth and direction are determined by a grid of holes made in the object(the distance between the holes, location of the drill holes relative to each other, the depth of drill holes) and the structural features of breakable objects.

Installation is a mobile device that can be transported from one destructed object to another. PDT of durable objects destruction has several advantages over the use of explosives, namely: the possibility of controlling energy consumption during objects destruction; absence of brisance that excludes scattering of splinters; absence of harmful substances excretion during destruction; providing a predetermined aimed spalling.

2.5 PDT of cleaning the hulls of ships and fixed offshore platforms from biological fouling [7].

PDT of cleaning ship hulls allows cleaning siding afloat, without entering the vessel to the dock. This PDT is also used for cleaning fixed offshore platforms (FOP) from biological fouling. Technological unit (electrode) is mounted on the element of FOP support structure by divers, fixed on it with defined working gap relatively to fouling and then is connected to GPC. High voltage pulsed corona discharge in medium with high conductivity (sea water) creates pressure waves and high speed hydro streams that destroy biological fouling on support constructions of FOP. Electrodes are moved across processed surface in the longitudinal direction at a distance of 1500 mm. Then they are rotated by predetermined angle (from 30º to 6 º), and the electrodes are moved in the opposite direction. Then technological unit is relocated to new area and abovementioned operations are repeated. PDT of cleaning ship hulls and fixed offshore platforms from biological fouling provides the performance of at least 200 m^2/h; it is collapsible for staff; device is mobile, easy to operate. Device withstands the current standards of environmental control. Mechanisms and components of equipment have a high operational reliability and do not require frequent maintenance and replacement of consumables.

2.6 PDT of rods knockout and castings cleaning *[8]* is to use the power factors of high-voltage discharge in water between the special electrode and the surface of the casting. In this case the shock waves arise in fluid which destroy the rods and mixture baked-on to the casting, cleaning its surface. Destruction of material is possible when creating critical stress in it. Moreover, destruction efficiency depends only on the time during which this condition persists.

With regard to the factors of the electrical discharge in the liquid rods destruction occurs under the action of the stress waves generated by the shock waves, and due to the pressure of fluid flow generated by post-discharge processes. The role of each of these factors is determined by the physical properties of the material rods, characterized by their acoustic stiffness. Electrohydraulic devices are used for knockout of rods from steel, iron castings, castings of non-ferrous alloys. These devise can be used in a single, small-scale and commercial production. Their most appropriate application is knockout of rods from large and medium sized castings.

Advantages of PDT of rods knockout are that it provides high performance and efficiency, eliminates hard manual labor, and reduces dust in the air in foundries.

2.7 PDT of crushing and grinding of artificial materials [9, 10], obtained by chemical reduction and melting or by crystal growth. Such materials include fused silica, refractory carbides, metallurgical and monocrystalline silicon, superhard materials (diamonds, cubic boron nitride). PDT of crushing and grinding of artificial materials because of the action of the ED as a source of high energy density have the ability to control the process of disintegration and to produce a product with a given fractional composition while minimizing waste and pollution of metal hardware, can significantly reduce the capital and energy costs and has small dimensions of the equipment.

2.8 PDT of carbon nanomaterials synthesis** [11]**.

Under the influence of powerful electric discharge pulses in liquid hydrocarbons appears a region of high pressure and temperature, in which the destruction and decomposition of hydrocarbon molecules takes place The ultimate degradation products are carbon in the solid phase, and hydrogen as a gas. In this case, the carbon can be emitted in different allotropic forms. In the process of electrical discharge treatment the composition of the organic liquids does not change, but the decomposition of the molecules occurs to form a solid phase - hydrocarbon nanomaterials (HCNM), and hydrogen and gaseous hydrocarbons excrete. The dry powder output nonlinearly increases with the number of carbon atoms in the molecules of the organic liquid and linearly - with the increase in the specific energy input.

Electrical discharge treatment of organic liquids produces amorphous carbon, short-range order of which is determined by the degree of hybridization of carbon atoms and by molecular structure of the original liquid. Retaining the same degree of hybridization of carbon atoms after the discharge treatment is caused by the choice of single discharge energy and by and the ratio of the energy of C-C and C-H bond breaking the hydrocarbon molecules.

Obtained HCNM show hydrogen sorption, electrokinetic, magnetic, anti-friction and anti-wear properties. PDT of hydrocarbon nanomaterials synthesis by electric explosion and electric discharge treatment of condensed carbon-containing substances allow obtaining nanomaterials with different functional purpose:

- carbon nanomaterials, use of which as additives to the magnesium during the mechano-chemical synthesis leads to improved sorption kinetics of hydrogen and a significant decrease in hydrogenation temperature regimes;
- intelligent anti-friction and anti-wear carbon nanomaterials containing nanographite, amorphous carbon nanotubes and nanofibers, which are promising additives for motor oil, transmission fluid;
- nanocarbon materials with strong magnetic properties (the value of specific saturation magnetization reaches values close to typical ferromagnets - 57 $A \cdot m^2/kg$);
- carbon nanomaterials containing higher fullerenes and endometallfullerenes.

The advantages of hydrocarbon nanomaterials synthesis PDT are high performance, continuity and wastelessness of processes.

2.9. PDT of carbon nanomaterials (CNM) production by plasma-chemical synthesis from carbon-containing gases** [12]**.

The essence of the PDT of nanocarbon synthesis from gas carbonaceous raw material is to obtain a nonequilibrium plasma under the action of pulsed high frequency discharges and due to the high temperature and pressure gradients. As a result of this method of synthesis carbon nanomaterials have a low bulk density (13.4 kg/m^3) and high specific surface area (SBET ~ 80 m^2/g). Composition of synthesis products obtained by a high-frequency discharge-pulse method of the carbon-containing gas (a mixture of propane, butane, acetylene) is essentially uniform, up to 90% of the particles have a similar form of granules with dimensions of the order of 15 to 35 nm, the yield of pure nanocarbon is up to 35 g/(kVt·h). Synthesis products are characterized by high content of chemically pure carbon up to 99%, confirming the possibility to eliminate the laborious cleaning operation. PDT produces virtually the entire spectrum of known allotropes of nanocarbon including carbine and graphene.

2.10 PDT of obtaining highly wear-resistant metal-matrix composites, dispersion-hardened by nanoparticles [13].

PDT of obtaining highly wear-resistant metal- dispersion-hardened composites is based on the ability to effectively use the latest methods of influence of highly concentrated energy flows on disperse systems – dispersion, activation and synthesis of polydisperse micro (from 10^{-5} to 10^{-7} m) and nanosized (from 10^{-7} to 10^{-9} m) composite powders with their subsequent consolidation by relatively low-temperature method of spark plasma sintering. Through the use of effects of necessary disperse phases excretion during a high-voltage ED impact on elementary powders and their mixtures heterogeneity of the blend may be artificially created and the rate of grain growth may be influenced by high-speed method of spark plasma sintering.

PDT of obtaining highly wear-resistant metal-matrix composites, dispersion-hardened by nanoparticles is directed upon obtaining highly wear-resistant composites of "carbide steel" type and new composites with metal binders for products of structural and instrumental purpose, working in conditions of friction and high loads, such as details of oil and gas pumps, parts of metallurgical and mining equipment, amenable to significant wear (guide rollers of wire rolling mill, etc).

Fundamentally new compositions of highly wear-resistant dispersion-hardened materials, based primarily on the domestic resource base, in particular – on iron, titanium, large reserves of which are located in Ukraine that provides a significant level of export replaceability of raw materials, are developed.

The advantages of PDT processing methods should include the increase of both strength and wear resistance of materials (by 30-60% or more) due to the fact that unlike conventional methods, the disperse reinforcement particles are not mechanically introduced into the powder mixture as an additional component in the blending of powders, but instead are generated by a reaction with an electric synthesis during ED processing of elemental powders and mixtures thereof in a hydrocarbon liquid. This provides not only a high degree of dispersion, but also significantly higher strength of adhesive bond between reinforcing microparticles and the base material.

Using a high-speed heating and lower maximum temperature holding time during spark plasma sintering of polydisperse micro and nanoscale composite powders produces compacts with higher relative density and a finer structure than when using conventional sintering techniques such as hot pressing and hot isostatic pressing.

In IPPT NASU an experimental system for spark plasma sintering "Gefest-10" [14], which is based on the direct passage o of output current with a peak value of 1 kA (superposition of direct and alternating current of high frequency (10 kHz) through the powder composition, was developed . 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 of specimens section, so it preferably carries out heating of the peripheral portion. This compensates for the effect of the heat sink and aligns the temperature conditions in the cross section.

Developed technological methods allow us to offer to market a simplified flow diagram for production of multifunctional materials, dispersion-hardened by nanoparticles, which can be used to significantly improve the wear resistance and heat resistance of tools for different purposes, and structural materials for reactor steels with high heat resistance characteristics, engines for different purposes, etc.

3. Conclusion

The analysis of PDT used in oil production, engineering, instrumentation, metallurgy, chemical industry, mining complexes, etc is performed in present review.

The use of high voltage electric discharge in different mediums allows to impact both changes of geometrical size and the structure of objects in order to give it certain mechanical and physical properties.

The Institute of Pulse Processes and Technologies of NAS of Ukraine designed and tested in the industry more than 40 different pulsed discharge technological processes: stimulation of oil wells; synthesis of hydrocarbon nanomaterials; removing rods from castings; crushing and grinding of materials; destruction of oversized and old foundations; regeneration of molding compounds; preparation of structured liquids; dispersion of mineral environments; activation of water and cement mortar; hardening of machine parts and stamping; fixing the pipe ends in the tube sheets of heat exchangers; calibration; compaction of the powder material; metal forming (rolling, drawing, extruding); processing of salt slag; intensification of the processes of casting and solidification of metals and alloys, etc.

Evolution of PDT and creation of new electric discharge devices is directed upon development of new pulsed technological processes for processing and obtainment of new materials.

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