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Research of plasma-electrolyte discharge in the processes of obtaining metallic powders

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Abstract. The use of the plasma electrolyte process has never been considered as a simple, cheap and fast method of obtaining powders used in selective laser melting processes. Therefore, the adaptation of the plasma-electrolyte process to the production of metal powders used in additive production is an urgent task. The paper presents the results of studies of gas discharge parameters between a metal and liquid electrode in the processes of obtaining metallic iron powders. The discharge combustion conditions necessary for the formation of metal powders of micron size are determined. A possible mechanism for the formation of powder particles in a discharge plasma is proposed.

1. Introduction

The phenomenon of electric discharge between the metal and liquid electrodes has been of interest to researchers since the end of the XIX century. Interest was of a fundamental and applied nature. From a fundamental point of view, the case of burning a discharge between a metal anode and an electrolytic cathode is interesting from the point of view of studying charge transfer from an electrolyte solution to plasma. Even more interesting is the study of the mechanism for converting the electrical energy of a discharge into mechanical energy with the appearance of shock waves. From a practical point of view, it is possible to identify many areas: the production of oxide coatings, the purification of sewage, the micro-dimension processing of non-conducting objects, the formation of the microrelief of the surface of metals, the cleaning and modification of the surface (cyanidation, nitration), the heat treatment and hardening with increasing wear resistance, the preparation of nanostructures and particles, creation of plasma torches and new types of plasma chemical reactors.

Studies of plasma-electrolyte discharge on the thermal treatment of metal objects and on the production of metal nanoparticles show the possibility of obtaining metallic powders. The search for new methods for obtaining metallic powders used in selective laser melting (SLM) is an urgent task. Selective laser melting refers to one of the types of additive technology, when metal powder is applied layer by layer on the platform and its selective melting is performed with a laser [1]. This technology allows you to obtain complex geometric products, which previously couldn’t be produced by standard
production methods. To the powders used in SLM, a number of requirements are established: to have a
certain dispersed composition, the particles must be spherical, there must be no gas pores in the
powder. [2]. Unfortunately, modern technologies for producing powders, namely gas, water, plasma
with a rotating electrode, plasma in crossed flows and HF discharge of atomization, have a number of
disadvantages:

1) High scatter of particles from 1 to 200 μm. This requires an additional sieving
procedure.
2) The difficulty of transferring the plant to the production of another type of material.
3) High energy consumption.
4) Use of expensive equipment.

In the case of gas atomization, the sputtering of molten metal occurs in a supersonic jet of an inert
gas. Spraying is carried out in a liquid stream during water atomization. In the third case, an arc
discharge is ignited between the electrodes, and the electrode is rotated around its axis, which leads to
the spattering of the metal. In the fourth case, the metal rod is sprayed in crossed plasma streams. In
the fifth case, the pre-ground metal particles are passed through the installation with a high-frequency
induction or capacitive discharge, and as a result they are shaped into spheroids.

The idea of additive production is the rapid production of prototypes of products from the required
materials [3]. Therefore, the development of a new cheap method for obtaining metallic powders,
which is devoid of all the above-mentioned drawbacks and is capable of rapid replacement of metallic
material, is an urgent task. One solution is to use a gas discharge with liquid electrodes [4,5,6], this
method is simple and does not require expensive equipment.

To create a technology, it is necessary to investigate the parameters of a gas discharge during the
formation of metallic particles and to determine how the parameters of the gas discharge plasma affect
the physical phenomena of the formation of a part. Therefore, the aim of the work was to study the
plasma-electrolyte discharge and the mechanism of formation of metallic particles in plasma.

2. Main part

Burning discharge can occur both on the metal anode and the cathode, while the electrode can be
immersed in the liquid, and may be above it. The combination of all these conditions with the
variation in the shape of the current and the magnitude of the applied voltage gives a variety of options
for searching for micron-size powder production regimes. Our starting point for the studies was a
survey paper [7], which describes the main methods for obtaining metal nanoparticles and their oxides.
Based on this review, a list of possible research options was developed, the description of which is
given in Table 1. It is evident from the table that for the type of experiment No. 1 the active metal
electrode was the anode that was immersed in the electrolyte, and the voltage obtained after the
smoothing capacitive filter. In total eight types of experiments were singled out.
Table 1. Explanation of the types of experiment.

| Experiment Type Number | The electrode is immersed in the electrolyte | Electrode over electrolyte | Active electrode ANOD | Active electrode CATOD | Voltage form: smoothened | Form of voltage: pulsating |
|------------------------|--------------------------------------------|----------------------------|-----------------------|------------------------|------------------------|---------------------------|
| 1                      | +                                          | +                          | +                     | +                      |                        |                           |
| 2                      | +                                          | +                          | +                     | +                      |                        |                           |
| 3                      | +                                          | +                          | +                     |                        | +                      |                           |
| 4                      | +                                          | +                          | +                     |                        | +                      |                           |
| 5                      | +                                          | +                          | +                     |                        | +                      |                           |
| 6                      | +                                          | +                          | +                     |                        | +                      |                           |
| 7                      | +                                          | +                          | +                     |                        | +                      |                           |
| 8                      | +                                          | +                          | +                     |                        | +                      |                           |

Figure 1 shows the functional diagram of the experimental setup, which consists of an electric power supply system 1, an electrolytic bath 2, an electrode system 3, an oscilloscope 4, an additional resistance 5, a voltmeter 6, an ammeter 7, a thermocouple 8. Using the electrode system, the distance between the anode and the electrolyte solution was monitored. With the help of an oscilloscope 4, the shape of the applied voltage and current was monitored, the voltmeter and ammeter were used to measure the voltage and discharge current. Two power sources were used in the work: the first one is a DC power source with continuously variable voltage, provides regulated rectified voltage of various shapes, consists of a diode bridge (diodes SD 246) and a laboratory autotransformer of regulation type 1M with a voltage range from 1 to 250V (to the power supply, depending on the experimental conditions, a smoothing capacitive filter is connected (C = 1560 μF)), the second is a high-voltage direct current source with a smooth adjustment of the output voltage in the range from 0.4 to 3 kV and current 0 to 10 A. Measurement of voltage and discharge current was carried out using two digital universal measuring devices APPA 305 and APPA 109N, the relative error of measurement is 0.8%.

Figure 1. Diagram of the experimental setup.
Burning gas discharge occurs between a metal electrode made of steel grade 07X16Н4Д4Б-Ш or from copper and liquid electrolyte. As the electrolytic cathode, aqueous solutions of NaCl and K₂CO₃ were used with a concentration of 0.1-1% by weight. The resulting powder was washed with deionized water and dried in a drying oven. The morphology of the powder was studied using a scanning electron microscope Carl Zeiss EVO 50. The dispersion composition was determined by the sieve method with a set of sieves from 10 to 300 μm. The average sieving time was 30 minutes. Analysis of the chemical composition was determined with the aid of a scanning electron microscope attachment of an energy-dispersive electron-probe spectrometer Oxford Instruments Inca X-act.

Consider the group of experiments under the numbers 1,2,3,4. It is established that in the case of using an aqueous solution of NaCl under anodic polarization and a pulsating form of stress, the electrochemical dissolution process predominates without forming a metallic powder. In experiment No. 1, the formation of a vapor-air shell is observed, the process proceeds stationary, but the power input is insufficient to melt the electrode surface and form a powder. In cases Nos. 2 and 4, the formation of an ultradisperse metallic powder was observed. The formation of a metal powder is observed during anodic and cathodic polarization of the electrode in experiments 5, 6, 7, 8. However, the use of a pulsating voltage does not allow maintaining discharge combustion at inter-electrode distances greater than 0.5 mm. In the case of using a metal cathode, intense heat generation occurs, which leads to uncontrolled melting of the electrode without forming a powder. Thus, the most appropriate options for the production of metallic powders are experiments No. 2 and No. 5.

The current-voltage characteristic of experiment No. 2 is shown in Figure 2a, the active electrode was a copper cathode. At the initial moment, the process of classical electrolysis proceeds and a linear increase in the current intensity occurs with increasing voltage. The formation of a vapor-air shell occurs at voltages of 60-70 V, which surrounds the metal electrode. With increasing voltage, the area of the discharge burns on the surface of the electrode, and then the intensity of the glow. The formation of a copper metallic powder is observed at voltages above 130 V.

Studies of the combustion of a gas discharge between a metal electrode 07X16Н4Д4Б-Ш and liquid electrodes have shown the possibility of obtaining a spherical powder with the dispersion of particles from 0.5 to 40 μm. In the voltage range from 500 to 800 V, particles smaller than 40 μm in size with a productivity of 1 • 10⁻² g / s occur. Above this range, the electrode melts and the process for obtaining the powder ceases. When certain values of current and voltage are reached, the process of spraying the metal anode is observed, most of the powder enters the electrolytic cathode and crystallizes. In parallel, there is a process of evaporation of the liquid electrode.

The main parameters of plasma-electrolyte production of steel powder are voltage, current, discharge power, used for heat generation, physical and chemical properties of the metal anode. The power put into the discharge is determined by the current-voltage characteristic, on the basis of which it is possible to estimate the energy contribution. Figure 2b shows the current-voltage characteristic of the plasma-electrolyte process for three inter-electrode distances.
The significant effect on the discharge combustion process is exerted by the electrolyte concentration, it is established that the electric field strength decreases with increasing concentration. Therefore, for the stability of the results, solutions with a concentration of less than 1% were used.

The formation of the powder occurs when the surface temperature of the anode reaches the corresponding solidus temperature. When the liquidus temperature is reached, the electrode is melted and large drops of metal are formed. Proceeding from this, the powder can be produced in the temperature range of the anode - liquidus and solidus. An increase in temperature will lead to an increase in the productivity of the powder, but with an increase in the particle size of the powder. The productivity of the powder increases nonlinearly with increasing temperature. A linear increase in the average particle size with increasing anode temperature is established. The largest amount of powder is obtained by a size smaller than 40 μm. Figure 3 shows SEM images of the resulting powders. The powder has a spherical shape, the smallest particle size is 0.5 μm. The resulting powder is suitable for use in selective laser melting installations. However, further research is needed to increase the productivity of the process by increasing the anode area and determining the dynamic characteristics of the powder.
The formation of a metal powder occurs as a result of the fusion of its surface with plasma of gas discharge. The main factors influencing the production of powder are the power of the gas, the amount of thermal energy supplied to the surface of the electrode, and the energy of the ions bombarding the surface of the cathode, the amount of heat withdrawn from the system through the electrode. By changing all of the above factors, it is possible to control the rate of fusion of the electrode surface and the size of the resulting metallic particles.

3. Results
Studies of the combustion of a gas discharge between a submerged metallic copper cathode and a liquid anode have shown the possibility of obtaining an ultradisperse powder with a particle dispersion of 0.5 to 2 μm. It is established that with increasing time of burning of the discharge an increase in the dimensions of the powder particles is observed.

Studies of the combustion of a gas discharge between the metal anode 07Х16Н4Д4Б-III and a liquid cathode have shown the possibility of obtaining a spherical powder with the dispersion of particles from 0.5 to 40 μm. The analysis of the obtained SEM photographs shows similarity with the powder obtained by the gas atomization method. The influence of the gas discharge parameters on the productivity of the process and the size of the particles obtained is determined. In the voltage range from 500 to 800 V, particles smaller than 40 μm in size with a productivity of $1\cdot10^2$ g / s occur. Above this range, the electrode melts and the process for obtaining the powder ceases. The location of the metal electrode affects on the mechanism of particle formation and on the physicochemical processes occurring in the discharge.

The parameters of the plasma-electrolyte discharge at which the powder particles are formed are determined.

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