Investigation of CoCr micropowder obtaining process in gas discharge with liquid electrodes

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Abstract. Plasma technologies have a wide range of applications: from agriculture and the food industry to energy industry. Such widespread use is due to the properties of plasma and a wide variety of methods for its preparation. Also, in metallurgy, plasma is used as a source of thermal energy, capable of producing metal melting in a short time. The paper studies the process of obtaining a metal powder from a CoCr alloy in a gas discharge with liquid electrodes. The regularities describing the relationship between discharge parameters and properties of the powders obtained. The resulting powders can be used in Selective Laser Melting technology.

1. Introduction
Additive manufacturing technologies are actively used in medicine. This is due to the individual geometry of the installed implants and dental prostheses. As you know, in the manufacture of single products, additive technologies are economically viable. Materials approved for use in medicine shouldn’t cause toxic effects on the body, should be biocompatible and resistant to corrosion. Such materials include titanium and cobalt-chromium alloys. Standard manufacturing techniques for individual implants and dental prostheses are based on the use of milling or casting methods. The milling procedure requires a lot of time to create an algorithm for the milling cutter, especially for such complex medical devices as implants. Therefore, it is effective for mass production, but inefficient for a single production. Casting technology requires the creation of a cavity into which metal will be poured. To do this, you need to somehow make a preliminary model to create this cavity. Another drawback is the distortion of the geometry due to the uneven cooling rate. All of the above makes the Selective Laser Melting (SLM) technology attractive [1]. This is primarily due to the emergence of new materials for 3D printing of metal and ceramic products [2]. In SLM plants, powder materials are used that must satisfy the following requirements: have a certain dispersion composition, particles must be spherical. At the moment, there are several known technologies for producing metal powders used in SLM - gas, water, plasma with a rotating electrode, plasma in crossed flows and RF discharge atomization. The disadvantage of these technological productions is the high dispersion of particle sizes from 1 μm to 200 μm, which requires additional purification and separation, the difficulty of the installation switching to the production of another type of material, the high energy consumption of the process, the difficulty of controlling and removing particles of the nanometer
range, the use of expensive equipment. The concept of additive production implies an individual geometry of the product, as well as the possibility of using a wide range of materials [3]. Now the main constraints are the shortcomings of the production of powders and the difficulty of quickly switching from one type of metal to another. Thus, the next stage in the development of the SLM process is the creation of technologies for the production of micro and nanopowders, devoid of the above disadvantages. One solution is to use a gas discharge with liquid electrodes [4,5,6], this method is simple and doesn’t require expensive equipment. Therefore, in this work, the aim was to study the plasma-electrolyte process for producing powders of cobalt-chrome alloys used in medicine.

2. Main part
The possibility of obtaining a powder in a gas discharge with liquid electrodes is very interesting. Gas discharges with liquid electrodes have been studied sufficiently since the mid-19th century, and have been widely used in practice: the formation of surface microrelief, heat treatment of products, the formation of functional coatings, cleaning the surface of metals, sterilizing water, obtaining nanoparticles, etc. The discharge can burn both on the metal anode and the cathode, while the electrode can be immersed in a liquid, or it can be above it. The combination of all these conditions with a variation in the shape of the current and the magnitude of the applied voltage provides many options for finding modes for producing micron sized powders. A known method of dispersing a metal anode under the influence of a discharge plasma with an electrolytic cathode. The cylindrical anode is vertically located above the surface of the electrolyte - cathode. The formation of a metal powder begins when a discharge current of a certain value is reached. This current value linearly depends on the diameter of the anode. Therefore, the main universal parameter determining the process of metal powder formation is the current density at the anode. Based on this information, the installation was modernized, the functional diagram of which is shown in Figure 1. It consists of an electric power system 1, an electrolytic bath - 2, an electrode system - 3, an oscilloscope - 4, additional resistance - 5, a voltmeter - 6, an ammeter - 7, thermocouples - 8. Using the electrode system, the distance between the anode and the electrolyte solution was monitored. Using the oscilloscope 4, the shape of the applied voltage and current was controlled, and the voltage and discharge current were measured using a voltmeter and ammeter.

Figure 1. The experimental setup

Combustion of a gas discharge occurs between a cobalt-chrome alloy anode and an electrolytic cathode. The anode is a metal cylinder with a diameter of 3 mm, located above the surface of the
electrolyte at a height of 1 to 5 mm. As the electrolytic cathode, aqueous solutions of NaCl and Na$_2$CO$_3$ were used with a concentration of 0.1-1% by weight.

Upon reaching certain current and voltage values, a process of spraying the metal anode is observed, most of the powder enters the electrolytic cathode and crystallizes. In parallel, the process of evaporation of the liquid electrode. The resulting powder was washed with deionized water and dried in an oven. The dispersion composition was determined by sieve screening with a set of sieves from 10 to 300 microns. The average sieving time was 30 minutes.

Features of the physicochemical processes of plasma-electrolyte powder production are associated with plasma properties. This type of discharge is similar to arc and glow discharges. It should be understood that the main difference between these types of discharges is in the mechanism of electron emission from the cathode. This difference is manifested in various cathodic voltage drops.

The main parameters of plasma-electrolyte production of steel powder are voltage, current, discharge power, spent on heat generation, physical and chemical properties of the metal anode. The discharge power is determined by the current-voltage characteristic, on the basis of which the energy contribution can be estimated. Figure 2 shows the current-voltage characteristic of the plasma-electrolyte process for three interelectrode distances. The obtained current-voltage characteristics coincide with the data for the case with steel anodes. Thus, the anode material does not significantly affect the plasma itself, but only affects the sputtering process, since the melting and sputtering temperatures of the electrode depend on the type of material. Powder formation is observed in a narrow range of voltage and discharge currents. Namely, at low input powers, the sputtering of the metal electrode is not observed, since the heat released is spent on the evaporation of the electrolyte and anode temperature increase to 300 - 700°C. At higher input capacities, we observe a complete melting of the electrode and the formation of one large drop of metal at the bottom of the electrolytic chamber.

The electrolyte concentration has a significant effect on the combustion of the discharge; it has been 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.

Figure 3 shows a linear dependence of the change in the temperature of the anode with increasing discharge power.
The powder formation occurs when the anode surface temperature reaches the corresponding solidus temperature. When the liquidus temperature is reached, the electrode melts and large metal drops form. Based on this, the powder production can occur in the temperature range of the anode liquidus and solidus. An increase in temperature will lead to an increase in powder productivity, but with an increase powder particle size of the. It was found that the dependence of the powder productivity on the temperature of the anode has a nonlinear dependence and grows with increasing temperature. A linear increase in the average particle size with anode temperature increase was found. Figure 4 shows a histogram of the particle size distribution of the obtained powder. The largest amount of powder is obtained with a size less than 40 microns. The powder has a spherical shape, the smallest particle size was 0.5 microns. The resulting powder is suitable for use in selective laser fusion plants. However, it is necessary to conduct further research related to increasing the productivity of the process by increasing the anode area and determining the dynamic characteristics of the powder.

3. Conclusion

Studies of the combustion of a gas discharge between a metal electrode made of cobalt-chromium alloy and liquid electrodes showed the possibility of obtaining a spherical powder with a particle size of 0.5 to 40 microns. Analysis of the obtained SEM photographs shows similarity with the powder obtained by gas atomization. The influence of gas discharge parameters on the process productivity and the size of the resulting particles is determined. In the voltage range from 700 to 800 V, the formation of particles less than 40 microns in size with a productivity of $0.89 \cdot 10^{-2}$ g/s. Above this range, the electrode melts and the powder production process stops. The location of the metal electrode affects the physicochemical processes occurring in the discharge and the mechanism of particle formation.

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