Gas discharge combustion with a liquid tetrachloride electrode

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Abstract. Titanium powders are widely used in selective laser melting and electron beam melting technologies to create medical implants. However, powders of a certain fractional composition are suitable for these purposes. A gradual increase in the volume of manufactured products requires the creation of new cheap methods for obtaining metal powders. Plasma-chemical synthesis in titanium tetrachloride solution can be one of the new methods for producing powders. A feature of this method is the use of a gas discharge with liquid electrodes, as a liquid electrode and is a titanium tetrachloride solution. The aim of the work was to study the possibility of obtaining a metal powder and its rapid cooling in a liquid. The question of the influence of the discharge parameters on the formation of metal particles remains open. In this work, a study of a gas discharge with liquid electrodes under the conditions of anode and cathode modes is carried out. A gas discharge between a liquid electrolyte and a metal electrode is experimentally investigated in the voltage range of 300-1000V. The conditions under which a stable discharge column is formed and a metal powder is formed are established. The regularities of the change in the I–V characteristic of the discharge are determined depending on the interelectrode distance.

1. Introduction

The high demand of the modern world industry for titanium alloys [1,2,3] poses topical issues for manufacturers to reduce the cost of titanium products by developing new production processes, as well as introducing resource-saving technologies. The development of Additive Manufacturing (AM) made it possible to manufacture metal products by melting the powder and further obtaining a continuous solid-phase structure [4]. Additive manufacturing makes it possible to manufacture parts of complex geometric shapes, which are impossible to obtain using traditional methods. In addition, additive technologies can reduce the time required to obtain a finished product [5]. AM allow the use of a wide range of various metallic materials: nickel, titanium, aluminum alloys, cobalt-chromium, various steels, etc. With the help of AM, ready-made functional products with high mechanical properties can be obtained. The quality of the products obtained depends on many technological parameters of the process, the correct choice of which is a fundamental factor in obtaining the required properties.

Despite such clear advantages over standard technologies, there are many issues to be addressed. With selective laser melting, the formation of various defects is observed: the formation of cracks, the presence of porosity, distortion of geometry, overheating of individual sections of the product leads to the separation of the product from the platform. Eliminating all of these is a complex
task that includes the feedstock problem. The quality of the raw materials is very important for titanium alloys, this is due to the strong deformation of the additive part after the end of the printing process and the high price of titanium powder. Therefore, the development of new simple methods for obtaining titanium powder of a given dispersion is urgent.

Plasma electrolyte sputtering is one of the new methods for producing metal powders [6]. Which consists in using a gas discharge with liquid electrodes. In this case, a sputtered metal electrode is installed above a liquid electrolyte that serves as a cathode [7]. When the metal anode contacts the liquid cathode, the electric arc is initiated, and then the metal electrode rises vertically to a distance of 5 mm. from the electrolyte surface. When the arc burns, the metal anode melts and the metal is sprayed out under the action of the plasma [8]. The formation of liquid metal droplets is observed, which quickly crystallize in the electrolyte. In this work, the goal is to develop a similar alternative method for producing a powder, which consists in using a titanium tetrachloride solution.

2. Main part
The study is based on the assumption of the dissociative decomposition of titanium tetrachloride to atoms and radicals, followed by quenching of the decomposition products by their rapid cooling. At temperatures of 5000 K and above, more than 99% of titanium and chlorine are in the atomic state. Rapid cooling to room temperature can suppress the reverse oxidation reactions of titanium with chlorine.

Investigations of the parameters of the gas discharge and the possibility of obtaining powders of metallic titanium from titanium tetrachloride were carried out on a setup, the functional diagram of which is shown in Figure 1. It consists of a power supply system - 1, an electrolytic bath - 2, an electrode system - 3, an oscilloscope - 4, an additional resistance - 5, voltmeter - 6, ammeter - 7, thermocouple - 8. Using the electrode system, the distance between the anode and the electrolyte solution was controlled. Oscilloscope 4 was used to control the shape of the applied voltage and current, and the voltage and discharge current were measured with a voltmeter and ammeter.

![Figure 1. Experimental setup diagram.](image)

The combustion of a gas discharge occurs between a metal anode/cathode (depending on the mode) made of graphite. The graphite electrode is a cylinder 10 mm in diameter immersed to a depth of 1 to 5 mm in a titanium tetrachloride solution.

To understand the processes occurring at the plasma – liquid cathode interface, it is necessary to know the dependence of the cathode potential drop on the acidity of the electrolyte and pressure. Spectral studies showing the lines of intensities of elements entering the solution from the magnitude of the cathode drop and the acidity of the electrolyte can give an idea of the mechanism of charge
transfer and the properties of plasma. It was found that the magnitude of the cathode drop does not depend on the gas pressure. Measurements of the intensity of the spectral lines of metals dissolved in the electrolyte from the acidity of the electrolyte show that for more acidic electrolytes, the intensity can exceed tens of times.

The most efficient preparation of powder of metallic titanium or its hydride was observed using an atmosphere consisting of a mixture of argon, hydrogen, and TiCl₄ vapor. It was possible to achieve the maximum titanium yield of 35% (the ratio of the mass of the obtained powder to the mass of titanium introduced into the reactor in the composition of TiCl₄). The resulting powder was pyrophoric and could be removed from the receiver only in an argon atmosphere.

In the course of research, it was possible to obtain an ultradispersed titanium powder with a particle size of 10-2000 microns, including the supply of titanium tetrachloride from a liquid to a hydrogen plasma zone, cooling and condensation of the powder in a liquid medium. Particle size control is carried out by changing the direct current of the discharge in the range of 100-500 A.

The main factors affecting the dispersion of the products obtained are: the rate of the chemical reaction, the temperature and rate of its change, the presence of nucleation centers in the system, and the chemical rock of the crystallizing substance.

At temperatures of hydrogen thermal plasma, which significantly exceed the sublimation temperature of titanium tetrachloride, as a result of dissociation, a rapid increase in the concentration of atoms of the starting substance occurs. The partial pressure of the low-volatile substance exceeds its equilibrium pressure, as a result of which the formation of nuclei of the condensed phase begins. Steam supersaturation is reduced due to the formation or growth of new nuclei. With sufficiently rapid cooling of the system, supersaturation increases and, as a consequence, spontaneous bulk condensation occurs. The limiting stage of the crystallization process is the diffusion of the substance to the centers of crystallization, therefore, the growth of crystals is difficult and the predominant formation of centers of crystallization is observed without their further growth. In a significant volume of the vapor-gas phase, two processes occur simultaneously: the formation of new crystallization centers and the growth of the previously formed ones, which determine the polydisperse structure of the obtained products. The degree of supersaturation and the rate of crystallization can be increased by lowering the temperature. When a system with a high concentration of a substance is removed from the high-temperature region to the quenching zone, a sharp drop in temperature occurs and the system becomes highly supersaturated with respect to the new temperature.

At high quenching rates, small particles are formed, and at low rates, large ones. As the current that generates the plasma arc increases, the plasma temperature increases, which contributes to an increase in the titanium concentration in the gas phase.

3. Conclusions
The question of the nature of the discharge remains open. For the formation of a metal powder, it is necessary to burn an electric arc with a high energy input.

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References
[1] Cui C X, Hu B M, Zhao L C and Liu S J 2011 Mater. Des. 32 1684–1691.
[2] Khorev A I, Khorev M A 2005 Titanium 1 40-53.
[3] Ilyin A A, Kolachev B A, Polkin I S 2009 Titanium alloys. Composition, structure, properties: Handbook 520 p.
[4] Nan Kang, Pierre Coddet, Lucas Dembinski, Hanlin Liao, Christian Coddet 2017 Journal of Alloys and Compounds 691 316-322.
[5] Protasov C E, Khmyrov R S, Grigoriev S N, Gusarov A V 2017 *International Journal of Heat and Mass Transfer* **104** 665-674.

[6] Sander J, Hufenbach J, Giebeler L, Bleckmann M [et al.] 2017 *Scripta Materialia* **126** 41-44.

[7] Kashapov L, Kashapov N, Kashapov R 2013 *Journal of Physics: Conference Series* **479** 012011.

[8] Denisov D, Kashapov N, Kashapov R 2015 *IOP Conference Series: Materials Science and Engineering* **86** 012005.

[9] Kashapov L, Kashapov N, Kashapov R, Denisov D 2016 *Journal of Physics: Conference Series* **669** 012029.