Electrothermal processing of tantalum capacitor powders

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Abstract. A low-pressure arc discharger with the hollow cathode is a newly developed electrotechnological device for finely dispersed powders of particles having dimensions 50 micron and less. The discharger is useful for putting powder into a high reactive zone of a plasma column and for thermal and mechanical action on particles. In the NSTU, the plain scales of the splinter tantalum powder were gained experimentally. Based on the results of the experiments, several constructive solutions are proposed for the heating of powders with subsequent deformation of tantalum powder particles on the target.

1. Introduction

Vacuum plasma torches with hollow cathodes enable heating, melting and refinement of fine powder in plasma during the flight of particles from the area where they enter the plasma to the receiving device. The powder within the plasma becomes heated through the interaction with electrons and ions. Total energy flow on the particle is $10^6 \div 10^7$ W/m². Working pressure range is 0.1÷100 Pa, current is 7.5÷10 kA, voltage is 80÷100 V. The plasma forming gas used is argon. Due to the electrodynamic interaction of each powder particle with the magnetic field of the discharge column, the powder is concentrated in the axis of the discharge column and only moves within the plasma column. 100 % processing of the loaded power is ensured. The initial content of impurities can reach 3 % [1, 2].

2. Results of the experimental tantalum powder processing

As established by the probe measurements of the column structure, the density of the plasma decreases from the cathode end to the anode [3, 4]. The maximum density of the plasma is located within the active area inside the cathode [5-7]. To intensify the heat flow on a powder particle, a special ring cathode was designed in which the inner cylinder is shorter than the outer one by (0.5÷1) of the inner cylinder diameter. The outer cylinder has a diaphragm which serves as a security ring protecting the plasma from quick collapse. That results in a larger area of the interaction between the powder and the dense plasma. Figure 1 shows a photograph of a ring hollow cathode that ensures effective heating of powder materials in the plasma column.

Figure 2 shows a photograph of an experimental vacuum plasma installation with electromagnetic control over the plasma parameters in the discharge column. The magnetic field is created by coils with cores installed around the perimeter of the furnace [8-10].

The experiments have the following purposes besides the troubleshooting of the vacuum plasma installation and improvement of the technological process. The first purpose is the study of purity degree of the powder material. The second one is the investigation on how the geometrical shape of the particles
is affected by their impact with the target. Another part of the experiment is the study of the erosion which determines the cathode longevity and powder accumulation on the transport tube output. The accumulation leads to the tube being choked and the powder supply cut off.

The time of the particle being within the column varied within the range $10^{-5}–10^{-3}$ s. The dosage of the powders was controlled by the mode of the vibrator operation and the expenditure of a transporting gas (argon, argon mixed with hydrogen, nitrogen, etc.). The usage of argon has to do with the necessity of its deep purification (especially from oxygen and nitrogen). The usage of nitrogen in the transporting gas enables to organize the formation of nitrides and oxides on the surface of the particles. With the usage of hydrogen under intense heating, the powder is purged of oxygen. The powder hardens as it leaves the column (cooling speed is up to $10^4$ K/s), which gives it a fine-grained structure and leads to even distribution of the elements over the volume (according to the results of x-ray structural analysis).

During the processing of tantalum capacitor powders in vacuum discharge, agglomerates are produced. They are presented in the photographs in figure 3.

Grinding and sifting of the produced powders with grain sizes from 40 µm to 200 µm enabled to evaluate the reduction of impurities, specific surface area, surface area by air permeability, bulk density, fluidity of the obtained powders for every experiment under various operating currents. The improvement of the listed properties proved the new electric technology to be promising for the altering of the properties of powder materials on an industrial scale. Figure 4 shows the general design model of the electrotechnological process for the production of processed powders.
The manufactured powder has the following technical parameters: the maximal discharge current is 3000 A at arc voltage up to 80 V and installed power 300 kVA; the maximum plasma manufacturing flow rate of argon \( G_{p} \) is \( 5 \times 10^{-3} \) kg/s; the maximum transport flow rate of argon \( G_{t} \) is \( 5 \times 10^{-3} \) kg/s; the maximum external magnetic field is 0.1 T at solenoid current up to 50 A; the processed powder flow rate \( q_{p} \) is up to 1.2 kg/s; the pressure in the processing chamber is from 1 to 10 Pa. The capacitor powder of 5th class was experimentally refined in the ring cathode vacuum plasma furnace (VPF) at the discharge current from 1 to 2 kA, anode voltage from 35 to 40 V and pressure in the processing chamber from 1 to 10 Pa. The optimal powder flow rate is no more than 1 kg/s. The technological process in the VPF is controlled by the cathode-anode distance \( L \) influencing the arc length and by the target position influencing the length of the powder jet.

The experiment has the following scheme. The powder material is accelerated by the transport gas in the technological tube up to velocity 20÷200 m/s depending on the particle size and the gas flow rate. Hence the powder absorbs the kinetic energy sufficient for the powder to flow within the plasma jet emitted by the ring hollow cathode. The powder particles moving in the plasma are heated up to the temperature slightly lower than the melting temperature. As a result, the powder material becomes free of impurities. Discharge current is completely circuited by the anode. A portion of the accelerated plasma with the powder falls on the rotating conic water-cooled target which moves it by centrifugal force to the collector of the processed powder.

The experimental installation is equipped with a high-speed camera with 4000 frames/s picture frequency to diagnose the powder particles motion and with a spectrometer to measure the radiation intensity at various wave lengths. The radiation intensity is measured to determine the temperatures of the cathode and the particles.

The initial powders have been manufactured through the decomposition of hydrogenated tantalum ingots in a wet milling rod mill. They are splinter-shaped. There are no particles of spherical or plate shape. The particle size distribution of powders of the 3rd and 5th class is stated in table 1. The 3rd class powder particles are larger than the 5th class ones. The powders are not fluid. They stick to a glass surface.

| Powder fraction dimension, μm | < 5 | 5÷10 | 10÷20 | 20÷30 | 30÷40 | 40÷60 | > 60 |
|-------------------------------|-----|------|-------|-------|-------|-------|------|
| 3rd class powder, %           | 3   | 18   | 22    | 25    | 12    | 10    | 10   |
| 5th class powder, %           | 2   | 49   | 36    | 8     | 5     | -     | -    |

The movie camera observation of the particles motion in the plasma flow has shown that the powder particles move rectilinearly, and the basic mass of the particles has axial velocity. Small fraction particles are localized in the central part of the plasma flow and form the area of higher intensity luminescence. Not more than 10 % of large particles deviate from the axial direction at 10÷13 deg. The comparison of different modes has shown that the dimensions of the cross-section of the flow depend on the powder and transport gas flow rates. Small particles have less velocity depending on the transport gas flow rate, proper magnetic field of discharge and external field produced by the solenoid.

The results of the refinement of tantalum powder of the 3rd class are stated in table 2. It is shown that plasma processing of the powder reduces the content of the most kinds of impurities. The content of some impurities is reduced significantly.

The results of the processing of tantalum powder of the 5th class are stated in table 3.

After the deformation, the powders were photographed with an electronic microscope to study the effectiveness of mechanical deformation caused by the collision with the target. The noticeable dispersion of powder particle dimensions and masses has given an ambiguous result of the photographs analysis. The small fraction of less than 5 μm was melted completely in the plasma flow and formed spherical particles sticking to larger ones. The medium fraction of less than 10÷20 μm produced plates under the plastic deformation. The large fraction was melted only partially. The VPF power was sufficient to process the large fraction but the medium and small fractions were melted at 110 kW power.
producing agglomerated powder which, in turn, was transformed into the powder with an average fraction dimension 40÷60 µm. Thus, further experiments were aimed at the choice of optimal modes of arc discharge and arc dimensions.

| Table 2. Chemical composition of the 3\textsuperscript{rd} class tantalum powder. |
|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Maximum impurity content, % | Al   | Ca    | W     | Mo    | Zr    | C     | H\textsubscript{2} | N\textsubscript{2} | O\textsubscript{2} | Si   |
| Initial          | 0.001 | 0.002 | <0.01 | <0.01 | 0.0004 | 0.01  | 0.01          | 0.012            | 0.3   | 0.003 |
| After treatment  | 0.0009| 0.0008| <0.01 | <0.01 | 0.0004 | <0.009| <0.005      | 0.01            | 0.21  | 0.002 |

| Maximum impurity content, % | Fe  | Mn  | Mg  | Ni  | Cr  | Ti  | Sn  | Nb  | C  |
|------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|----|
| Initial                      | 0.005 | 0.0003 | 0.0003 | 0.003 | 0.003 | 0.003 | 0.0003 | 0.25 | 0.008 |
| After treatment              | 0.0035 | 0.00012 | <0.0002 | 0.0009 | 0.001 <0.0003 | 0.00015 | 0.2 | 0.009 |

| Table 3. Chemical composition of the 5\textsuperscript{th} class tantalum powder. |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Maximum impurity content, %   | Al   | Ca    | W     | Mo    | Zr    | C     | H\textsubscript{2} | N\textsubscript{2} | O\textsubscript{2} | Na  |
| Initial                      | 0.0005 | 0.003 | 0.003 | 0.001 | 0.0005 | 0.01 | <0.0001 | 0.012 | 0.35 | <0.0001 |
| After treatment              | <0.0003 | <0.0003 | 0.003 | 0.001 | <0.0005 | <0.01 | <0.0001 | <0.012 | <0.3 | <0.0001 |

| Maximum impurity content, %   | Si   | Fe   | Mn   | H\textsubscript{2} | Ni  | Cr  | Ti  | Sn  | Nb  | Cu  |
|------------------------------|-----|-----|-----|-------------------|-----|-----|-----|-----|-----|-----|
| Initial                      | 0.002 | 0.002 | 0.0005 | 0.01 | 0.001 | 0.0005 | 0.001 | 0.0005 | 0.02 | 0.001 |
| After treatment              | 0.001 | 0.0019 | 0.00012 | <0.01 | 0.0006 | 0.0004 | <0.0009 | 0.0002 | 0.018 | 0.0006 |

**Figure 5.** Photo of the 3\textsuperscript{rd} class raw a) and processed b) tantalic powder (scale of magnification 2500).

**Figure 6.** Photo of the 5\textsuperscript{th} class raw a) and processed b) tantalic powder (scale of magnification 2500).
Figure 5 shows the photographs allowing to trace the change of the particle size distribution in powders of the 3rd class after processing. Discharge power was 45 kW, the powder flow rate 1 kg/h, the transport gas flow rate 2·10^{-6} kg/s. Figure 6 shows the photographs allowing to trace the change of the particle size distribution in powders of the 5th class after processing. Discharge power was 50 kW, the powder flow rate 0.8 kg/h, the transport gas flow rate 2·10^{-6} kg/s.

3. Conclusion
The new construction of a cathode unit enabled to raise the temperature of the processed powder material up to 3500 °C. The plasma processing of the powder reduces the content of the most kinds of impurities. The content of some impurities is reduced significantly. As the melted tantalum powder hits the conical target, its particles are flattened, which enlarges their area and therefore increases the capacity of condensers.

References
[1] Cherednichenko A V and Cherednichenko M V 2000 The vacuum plasma electric furnace for industrial raw powder melting of tantalum ingots from thermo-sodium Proc. 5th International Conference on Actual Problems of Electronic Instrument Engineering (Novosibirsk, Russia) vol 913083 pp 35-36
[2] Anshakov A S, Aliferov A I and Urbach A E 2008 Arc plasma generator for deposition of powder coatings Proc. of the 3rd international forum on strategic technologies (Novosibirsk, Russia) vol 4602844 pp 378-382
[3] Galkin S G and Cherednichenko M V 2002 Experimental characteristics of vacuum arc discharge inside the hollow cathode Proc. of the 6th Russian-Korean International Symposium on Science and Technology (Novosibirsk, Russia) vol 1028002 pp 219-221
[4] Cherednichenko M V, Serikov V A, Butakov E B and Urbakh A E 2017 Erosion of plasma generator electrodes for various power supplies Russian Metallurgy (Metally) 6 527-531
[5] An'shakov A S and Urbakh E K 1999 Modeling of the thermal effect of an arc cathode spot electrode erosion Proc. of the 3rd Russian-Korean International Symposium on Science and Technology (Novosibirsk, Russia) vol 2,876206 pp 479-482
[6] An'shakov A S, Zhukov M F and Timoshevskii A N 1975 Dynamics of electrical parameters of an arc and its behavior in a plasmatron channel Journal of Applied Mechanics and Technical Physics 14(5) 612-616
[7] Cherednichenko M V, Galkin S G and Kosinov V A 2002 The vacuum plasma electric furnace for industrial melting of tantalum ingots Proc. of the 6th Russian-Korean International Symposium on Science and Technology (Novosibirsk, Russia) vol 1028003 pp 222-225
[8] Yudin B I 2004 New electrotechnologies of processing of powder materials Proc. of the 7th International Conference on Actual Problems of Electronic Instrument Engineering (Novosibirsk, Russia) vol 1427177 pp 31-36
[9] Cherednichenko M V, Gramolin A V and Shkret S P 2003 Matching of power supply parameters and electrical working modes of vacuum plasmotrons with hollow cathodes Elektrotekhnika 9 48-53
[10] An'shakov A S, Urbakh E K, Radko S I, Urbakh A E and Faleev V A 2015 Electric-arc steam plasma generator Thermophysics and Aeromechanics 22(1) 95-104