

A Plasma Reactor for the Synthesis of High-Temperature Materials: Electro Thermal, Processing and Service Life Characteristics

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Abstract. The three-jet direct-flow plasma reactor with a channel diameter of 0.054 m was studied in terms of service life, thermal, technical, and functional capabilities. It was established that the near-optimal combination of thermal efficiency, required specific enthalpy of the plasma-forming gas and its mass flow rate is achieved at a reactor power of 150 kW. The bulk temperature of plasma flow over the reactor of 12 gauges long varies within 5500÷3200 K and the wall temperature within 1900÷850 K, when a cylinder from zirconium dioxide of 0.005 m thick is used to thermally insulate the reactor. The specific electric power reaches a high of 1214 MW/m³. The rated service life of electrodes is 4700 hours for a copper anode and 111 hours for a tungsten cathode. The projected contamination of carbides and borides with electrode-erosion products doesn't exceed 0.0001% of copper and 0.00002% of tungsten.

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1. Introduction

Processing capabilities currently used for producing and utilizing refractory metals and their chemical compounds, including those in nano- and ultra-dispersed sizes specified, are expanding [1 - 3]. Considerable experience is gained at Siberian State Industrial University relating to research and utiliza-



tion of three-jet direct-flow plasma reactors with nitrogen-operated arc plasma torches (plasmatrons), and their application in the synthesis of refractory carbides, borides and their compositions, as summarized in the works in reference [4 - 9]. Thus, it is shown that the optimum reactor design should be a structure with evenly spaced plasma torches around the circumference, wherein their plasma jets have an angle of 30-45 degrees to the axis of the reactor; and thermal protection with intensely cooled walls, ensuring a maximum life of the mixing chamber, high and uniform radial temperature distribution and rates with a minimal loss of thermal energy. In fact, the research, by using the sectional calorimetric measurement of energy balances in reactors with an inner diameter of 0.046 m and mixing chambers with different angles of plasma jets, shows [8] that, when an angle of plasma jets inclining to the reactor axis decreases from 90 to 30 degrees, the density of heat flow in the mixing chamber is reduced almost three times that results in its longer service life. However, along with that in both cases, at the initial section of 4-5 gauges long, the heat flow to the walls is characterized by high density that greatly reduces the reactor's capacity in terms of dispersed material heating and evaporating. Heat losses in the reactor can be reduced by lining its channel with a heat insulating material. The applied silica-based skull lining allows the wall temperature to rise, the value of which depends on the power of arc discharge [8]. Thus, with an arc discharge power of 50 kW, the wall temperature at a length of 8 gauges varies from 1600 to 900 K, and in the absence of heat insulation - from 970 to 400 K. Building a "hot" wall helps reduce the heat flow intensity by 15-20% in the average and the temperature factor by 100%, and increase the bulk temperature of the exchange gas by 13% in the mostly heat-stressed zone of the reactor.

Heat transfer in the channel of the plasma reactor has been investigated at values of the Reynolds numbers equal to 700-1500 [4 - 9], taking into account the effect of induced turbulence in the plasma flow, the outflow of heat from plasma to the dispersed raw material and the formation of skull lining or the use of lining on the channel walls in the reactor. For the reactor channel, it is established that the intensity of heat exchange is high within the initial section of up to 4 gauges long, typical for turbulent conditions; criteria-related dependences are obtained for calculating heat-exchange coefficients for the conditions of raw material introducing into the flow.

However, the summarized in [4 - 9] results have been obtained for a laboratory plasma reactor with a capacity of 30-50 kW, information on its thermal, technical and processing characteristics is not complete, the findings do not have process design proposals and recommendations with reference to the scaling up to the industrial level. In this connection, this paper is dedicated to the following issues:

- 1) Specifying a power of the three-jet reactor to be used at the industrial level, and structural and technical conditions for achieving the target;
- 2) Determining a bulk temperature of plasma flow;
- 3) Determining a specific electric capacity of the mixing chamber;
- 4) Determining a service life of plasma torches;
- 5) Evaluating the contamination of refractory compounds with erosion products from plasma torch electrodes.

2. Results and discussion

Specifying a power of the three-jet reactor to be used at the industrial level

The following limitations are taken into account when dealing with this issue:

- the specific enthalpy of plasma flow at the reactor inlet should be 7.5-8.5 MJ/kg for efficient dispersed material processing [10];
- the initial speed of plasma flow should not exceed 60-65 m/s [11];
- for plasma generating, the plasma torches should be used with an electric arc that stabilized by gas vortex, since solenoids are structurally and technically difficult to install;
- the plasma torches should operate on a mixture of nitrogen and hydrogen.

The main performance characteristics of plasma torches, potentially suitable for three-jet reactors are shown in Table 1. Comparison of characteristics shows that the plasma torches of EDP-104A and EDP- 114 types are mostly appropriate. A growth in power of these plasma torches is achieved, as a rule, by increasing in the arc current and voltage under conditions of a simultaneous increase in the

consumption of plasma-forming gas. It should be noted that there is a clear intention to use technology and ensure the reactor operation at the minimum permissible flow of the plasma-forming gas, usually no more than 50-65% of the maximum possible. This condition combined with higher values of current predetermines a decrease in the thermal efficiency of plasma torches with increasing the power.

Table 1. Main performance characteristics of plasma torches, potentially suitable for three-jet- reactors [11 - 12]

| Performance Characteristics | Types of plasma torches | | |
|----------------------------------|--|--|---|
| | EDP-104A | EDP-119 | EDP-114 |
| Gas | Nitrogen, mixed nitrogen and hydrogen. | Nitrogen, hydrogen, mixed nitrogen and hydrogen. | Nitrogen, hydrogen, mixed nitrogen and hydrogen |
| Gas consumption kg/s | | $(6 \div 8)10^{-3}$ | $(6 \div 8)10^{-3}$ |
| Thermal efficiency | $(1 \div 5)10^{-3}$ | $0.5 \div 0.7$ | $(6 \div 8)10^{-3}$ |
| Current, A, max | $0.5 \div 0.8$ | 400 | $0.5 \div 0.7$ |
| Arc voltage, V, max | 200 | 500 | 400 |
| Power, kW, max | 250 | 200 | 500 |
| Gas heating temperature, K, max | 50 | 5000 | 200 |
| Nitrogen | 5500 | | 5500 |
| Stabilization of electric arc | | magnetic | |
| Tungsten cathode service life, h | Gas vortex, magnetic | 100 | Gas vortex, magnetic |
| Copper anode service life, h | | 500 | |
| Overall length, m | 100 | 0.25 | 100 |
| Mass, kg | 500 | 4.80 | 500 |
| | 0.21 | | 0.30 |
| | 1.45 | | 5.50 |

Figure 1 gives the values of thermal efficiency for reactors with a power of 30, 50, 80, 120 150 kW and the EDP-104A plasma torches, and reactors with a power of 200, 250 kW and the EDP-114 plasma torches. The values were obtained experimentally by using the calorimetric measurements of sections and projected by calculating in accordance with recommendations in [9]. As it is seen from the table, the thermal efficiency of the plasma torches is close to 0.50 when a power of 150-250 kW is specified for commercial scale reactors. The specific enthalpy values are achieved with the plasma torches having a power of 80-150 kW, which is required for plasma metallurgy to produce refractory compounds. With this, an increase in power from 80 to 150 kW results in a doubling of mass of the generated gas with reference to the required level of enthalpy.

Thus, the near-optimal combination of thermal efficiency, specific enthalpy of the plasma-forming gas required and its mass flow rate is achieved with the reactor of 150 kW in power. Further increasing the power level is irrelevant, because the designs of plasma torches available for selection do not provide the desired specific enthalpy level of plasma flow.

Determining a bulk temperature of plasma flow

To protect the walls of the reactor channel and reduce the size of a near-wall low temperature zone, the reactor channel was lined using zirconia cylindrical inserts with a wall thickness of 0.005 m and an outside diameter of 0.064 m, reducing its diameter to 0.054 m.

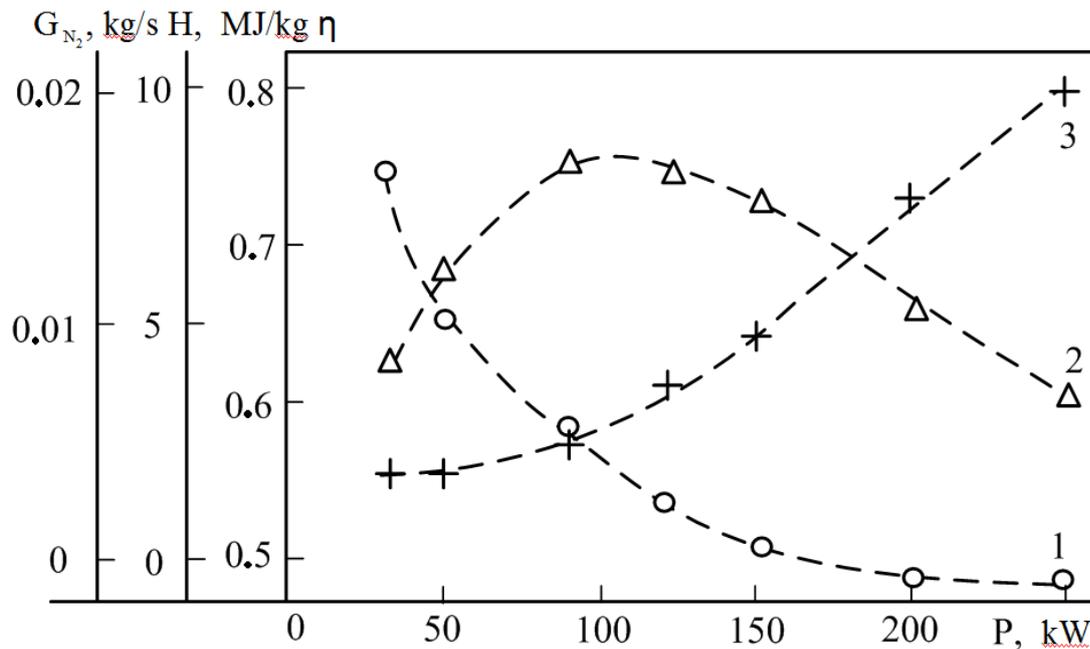


Figure 1 - Dependence of the thermal efficiency (η , 1), the specific enthalpy of plasma flow at the reactor inlet (H, 2), the mass flow of the plasma-forming gas (G_{N_2} , 3) on the reactor power

Selection of zirconia as a heat insulating material is determined by its properties such as refractory quality (a melting point of 2963K), low thermal conductivity (the coefficient of thermal conductivity is 0.42-2.63 W/(m·K) at a temperature of 2173 K) and high chemical resistance under the conditions of reactions taking place in the plasma reactor.

We investigated the longitudinal distribution of heat flow, the bulk temperature, and internal surface temperatures of the lined and unlined reactor walls to evaluate experimentally how the thermal protection shield made of zirconium dioxide is effective in protecting the lined and unlined walls of the reactor with a 150 kW power at a mass flow of nitrogen equal to 0.009 kg/s, using the sectional calorimetry. The diameter of the unlined reactor channel was 0.054 m. The heat flow in each section was determined in terms of heat balance by measuring the heating of cooling water. The inaccuracy of values calculated by using calorimetry is $\pm 10\%$ and caused by errors of flow meters calibration ($\pm 3\%$), the heat flow determination ($\pm 4\%$) and calculation ($\pm 3\%$).

The distribution of bulk temperature in the plasma flow along the reactor length was calculated in terms of a value of bulk enthalpy. In this case, the enthalpy of the gas flow at the section outlet was less than at the inlet by the amount of energy the gas transferred to the walls of this section. The bulk enthalpy was calculated as the arithmetic mean of the input and output values of enthalpy. The internal surface temperatures of lining and the unlined reactor walls were calculated using the experimentally observed values of heat flow.

The main results of research are presented in Figures 2 and 3. It can be seen that the use of lining from zirconia provides the increased flow bulk temperature and wall temperature: along the reactor of 12 gauges, the bulk temperature changes from 5500 K to 3200 K in the case (1) and 2650 K in the case (2), and the wall temperature changes within 1900-850 K and 800-350 K respectively.

Determining a specific electric capacity of the mixing chamber

The specific electric capacity, defined as the ratio of power supplied to the reaction zone to its volume, is an essential characteristic of modern electric and thermal equipment and varies between a value of

0.2 MW/m³, which is representative for the majority of electric furnaces, and a very high value of 3750 MW/m³, which is specific for high pressure reaction chambers in the diamond synthesis [13].

The specific electric capacity is defined as

$$W_{sp} = \frac{P}{V_{r.z.}} = \frac{P_o \cdot \eta}{0.785 \cdot D_r^2 \cdot L_{r.z.}}, \quad (1)$$

Where W_{sp} is the specific electric capacity, MW/m³;

P_o is the total power, kW;

D_r is the internal diameter of the reactor channel, m;

$L_{r.z.}$ is the length of the reaction zone, m;

P is the power supplied to the mixing chamber, kW;

$V_{r.z.}$ is the volume of the reaction zone, m³;

η is the thermal efficiency of the plasma torches.

At the same time, the thermal efficiency of the plasma torches was determined based on the results of calorimetry; the length of the zone, where the dispersed material evaporated, the pyrolysis of hydrocarbons occurred and the reacting mixture of a given composition formed, (the so-called "reaction zone") was assumed to be a 0.5 gauge according to the results of simulating interaction between the plasma and material flows [9]. The values of specific electric capacity are 625, 688, 813 and 1214 MW/m³ that calculated for the reactor channel with a diameter of 0.054 m, insulated with zirconium dioxide, and plasma torches with a power of 85, 100, 125, 150 kW respectively, which are significantly higher than for traditional electric and thermal equipment.

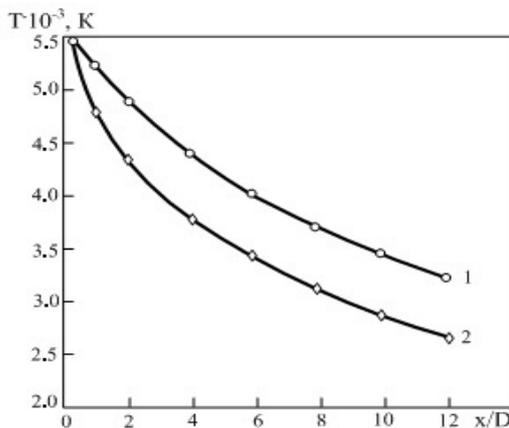


Figure 2 - (T(1) = (5500 ÷ 3200) ± (100 ÷ 60); T(2) = (5500 ÷ 2650) ± (100 ÷ 55)). Longitudinal distribution of bulk temperature for the reactor lined with zirconium dioxide (1) and the unlined reactor (2)

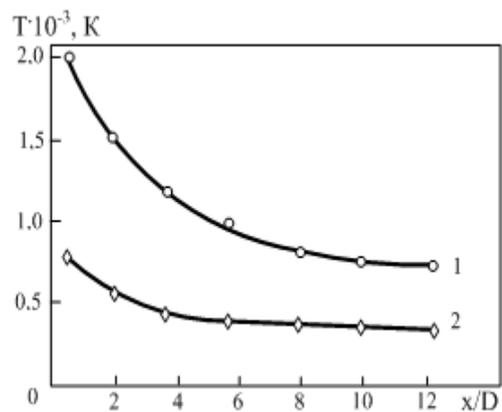


Figure 3 - (T(1) = (1900 ÷ 850) ± (35 ÷ 15); T(2) = (800 ÷ 350) ± (10 ÷ 5)). Longitudinal temperature distribution over the internal surface of zirconia lining (1), unlined walls of the reactor (2)

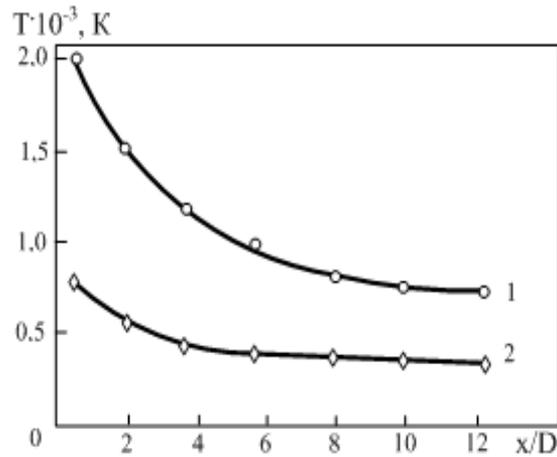


Figure 3 - $(T(1) = (1900 \div 850) \pm (35 \div 15))$; $T(2) = (800 \div 350) \pm (10 \div 5)$.

Longitudinal temperature distribution over the internal surface of zirconia lining (1), unlined walls of the reactor (2)

Determining a service life of plasma torches

Service life of a plasma torch defined by erosion of electrode materials is its most important feature. Cathode and anode spots of arcs ignited with cold electrodes are characterized by the extremely high density of heat flow that reaches $104\text{-}105 \text{ MW/m}^3$ [12]. Any of known materials is not able to withstand such thermal loads in steady-state conditions. In order to ensure an acceptable level of electrode erosion, near-electrode areas of the arc are moved over the electrode surface by applying aero or electro dynamic forces to those areas. When moving the arc spot, the electrode surfaces is subjected to cyclic thermal shocks, causing the appearance of cracks in the electrode material, resulting in its mechanical failure and reduction in thermal and electrical conductivity. Therefore, the rate of electrode erosion is dependent on physical processes, occurring in the near-electrode areas of the arc discharge, on the electrode surface and inside a crystal lattice of the metal the electrode is made of. It is determined by such transient processes as large- and small-scale arc bridging, the influence of external magnetic field on an arc column, aerodynamics of gas flow in the plasma torch. The cathode erosion also depends on its diameter and design, a composition of plasma gas, amperage, cycles of operation (quantity of plasma torch switching on), quality of thermal contact between a tungsten rod surface and copper cathode holder [12]. Erosion of a copper anode is determined by such factors as conditions of arc cooling, amperage, magnetic strength, and protection of the anode surface with inert or natural gas [12]. An integral characteristic of the electrode erosion processes is specific erosion, measured in kg/C that, of course, does not reveal details of micro processes occurring and their influence, oxide films on the surface of electrodes, thermal stresses in the metal, and features of motion of the arc spots. The specific erosion value varies within $(2\div 5) \cdot 10^{-12} \text{ kg/C}$ for the tungsten cathode in nitrogen at the atmospheric pressure and a concentration of oxygen up to 0.5% and a current of 250-300 A. When the concentration of oxygen increases up to 1.5%, the specific erosion value is as high as $(2\div 4) \cdot 10^{-8} \text{ kg/C}$. The specific erosion value of the cylindrical copper anode is also largely determined by oxygen presenting in the working gas. Thus, with a current of 180 A in high purity nitrogen containing about 0.001% oxygen, the specific erosion is $10^{-12}\div 10^{-11} \text{ kg/C}$, and it increases by more than an order of magnitude in technical purity nitrogen (0.5% of oxygen).

Service life of a plasma torch is normally assumed as equal to a minor value of service life specified for one of the electrodes. Determining a service life of electrodes experimentally is time-

consuming and expensive. Therefore, the service life of the anode and cathode was estimated by calculation. For this purpose, we assumed that a convoluted profile of the worn out anode in place of arc bridging behind the shoulder is similar to a triangle (Figure 4 a), and the diameter of a crater formed on the cathode surface by the arc evaporation process is equal to the diameter of the arc bridging place (Figure 4 b).

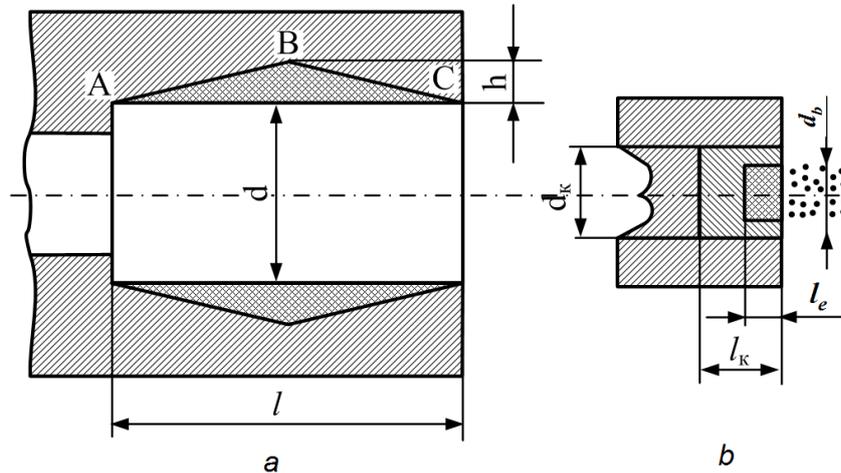


Figure 4 - Geometric models for calculating the service life of anodes (a) and cathodes (b)

The volume of the anode material removed by erosion is defined as follows in m^3

$$V_e = 0,5 \cdot h \cdot \pi \cdot l(d + h) . \quad (2)$$

It is assumed, that $l = 5.0 \cdot 10^{-2}$ m; $h = 0.2 \cdot 10^{-2}$ m; $d = 1 \cdot 10^{-2}$ m, then

$$V_e = 0.5 \cdot 0.2 \cdot 10^{-2} \cdot 3.14 \cdot 5 \cdot 10^{-2} (1 \cdot 10^{-2} + 0.2 \cdot 10^{-2}) = 1.88 \cdot 10^{-6} m^3 .$$

The time of continuous operation for the copper anode is

$$t_a = \frac{\rho_a \cdot V_a}{G_a \cdot I} , \quad (3)$$

Where ρ_a is the density of the anode material, $\rho_a = 8.9 \cdot 10^{-3}$ kg/m³;

G_a is the specific erosion of the anode, $G_a = 5 \cdot 10^{-12}$ kg/C;

I is the arc amperage, A . $I = 200$ A.

$$t = \frac{8.9 \cdot 10^{-3} \cdot 1.88 \cdot 10^{-6}}{5 \cdot 10^{-12} \cdot 200} = 4700 \text{ h}$$

For the cathode, it is assumed that the diameter of the tungsten insert equals $d_k = 0.3 \cdot 10^{-2}$ m, the length of the insert $l_k \leq d_k$ is $0.3 \cdot 10^{-2}$ m, the permissible depth of the cathode erosion is $l_e = 0.3 l_k$. Then $l_e = 0.3 \cdot 0.3 \cdot 10^{-2} = 0.1 \cdot 10^{-2}$ m.

It is assumed that the diameter of the crater, formed on the cathode as a result of arc effect, is equal to the diameter of arc bridging

$$d_b = B \cdot I^{0.5} , \quad (4)$$

Where B is the coefficient; for nitrogen it is equal to $1.6 \cdot 10^{-4}$ [7].

Then $d_b = 2.6 \cdot 10^{-4} \cdot 200^{0.5} = 2.3 \cdot 10^{-3}$ m.

The volume of the material removed by erosion is

$$V_e = \frac{\pi d_b^2 \cdot l_e}{4} = \frac{3.14 \cdot (2.3 \cdot 10^{-3})^2 \cdot 0.1 \cdot 10^{-2}}{4} = 0.42 \cdot 10^{-8} m^3 .$$

Taking into account $\rho_k = 19.34 \cdot 10^3$ kg/m³ for tungsten and assuming $G_k = 1 \cdot 10^{-12}$ kg/C, we obtain

$$t_k = \frac{19 \cdot 34 \cdot 10^3 \cdot 0.42 \cdot 10^{-8}}{1 \cdot 10^{-12} \cdot 200} = 4.01 \cdot 10^5 \text{ sec.} = 111 \text{ hr.}$$

Consequently, the continuous operation of the plasma torch is determined by the service life of the cathode and exceeds 100 hours that corresponds to the specification. However, it should be noted that the specific erosion values relative to anodes and cathodes are taken for the conditions when a natural gas is added to the plasma gas (technical purity nitrogen) to bind oxygen and protect electrodes, and this contributes to the reasonability to employ this technological method with the purpose of increasing the service life of electrodes.

Evaluating the contamination of refractory compounds with erosion products from torch electrodes

Currently, in the related technical literature there is an opinion widely accepted that the arc plasma torches have their limited use in plasma reactors because of the strong contamination of the produced materials with the products of the electrode-related erosion, i.e. tungsten from cathodes and copper from anodes [12]. In this connection, the study was performed to evaluate possible contamination of refractory compounds with electrode erosion products for the following conditions: the carbide or boride reactor output is 3.0 kg/h, the specific erosion of the copper anode is $5 \cdot 10^{-12}$ kg/C, the specific erosion of the tungsten cathode is $1 \cdot 10^{-12}$ kg/C, the service life is 4700 and 111 hours for the anode and cathode respectively. Then the mass of erosion products formed in an hour makes, for the copper anode:

$$m_{Cu} = \frac{8.9 \cdot 10^3 \cdot 1.88 \cdot 10^{-6}}{4700} = 3.6 \cdot 10^{-6} \text{ kg ,}$$

For the tungsten cathode:

$$m_W = \frac{19 \cdot 34 \cdot 10^3 \cdot 0.42 \cdot 10^{-8}}{111} = 7.2 \cdot 10^{-7} \text{ kg ,}$$

that corresponds to the content of copper $\frac{0.0036}{3000 + 0.0036} \cdot 100 \% = 0.0001 \%$, and tungsten

$$\frac{0.00072}{3000 + 0.00072} \cdot 100 \% = 0.00002 \% \text{ in the carbide.}$$

According to the obtained values, there is no actual threat of contaminating refractory compounds with tungsten and copper impurities and reducing their useful properties in this regard.

3. Conclusions

The three-jet direct-flow plasma reactor with a channel diameter of 0.054 m was studied in terms of service life, thermal, technical, and functional capabilities. It was established that the near-optimal combination of thermal efficiency, required specific enthalpy of the plasma-forming gas and its mass flow rate is achieved when the reactor has a power of 150 kW. The bulk temperature of plasma flow over the reactor of 12 gauges long varies within 5500÷3200 K and the wall temperature within 1900÷850 K, when a cylinder from zirconium dioxide of 0.005 m thick is used to thermally insulate the reactor. The specific electric power reaches a high of 1214 MW/m³. The rated service life of electrodes is 4700 hours for a copper anode and 111 hours for a tungsten cathode. The projected contamination of carbides and borides with electrode-erosion products doesn't exceed 0.0001% of copper and 0.00002% of tungsten.

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