Technological basis of the plasma-metallurgical production of zirconium carbide

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Abstract. Based on the interpretation of the results of theoretical and experimental studies, a continuous technological process for zirconium carbide production in the plasma-metallurgical reactor, including plasma generation, plasma processing of zirconium-carbon-containing raw materials, the formation of ZrC, forced cooling and its separation from the process gases flow leaving the reactor, was developed.

1. Introduction
Zirconium carbide ZrC, investigated and put into circulation by the scientific school of the famous Russian material scientist G.V. Samsonov more than 50 years ago, is still in demand in the technology of various materials: cermet tool and construction materials, refractory and abrasive, for the modification of coatings [1 - 6]. The analysis of modern scientific and technical information reflects the trend of the transition from the use of coarse-grained zirconium carbide to micro- and nanocrystalline, which is due to the desire of scientists and technologists to achieve a qualitatively new level of operational properties of materials and coatings based on it.

The basis of modern production of zirconium carbide is the carbothermic method. The carbothermic method is implemented in several technological options and is used to obtain zirconium carbide when used as part of materials for abrasive processing, spraying and surfacing, protective coatings. However, the strategically important nanocrystalline zirconium carbide market segment is completely closed by foreign suppliers, including companies such as Nanostructured & Amorphous Materials, Inc. (USA), Hefei Kaier Nanotechnology & Development Ltd. Co (China), NEOMAT Co (Latvia), PlasmaChem GmbH (Germany). This necessitates the development of Russian nanotechnology of zirconium carbide.

In this regard, the study and technological implementation of carbide formation processes during the plasma-chemical processing of zirconium-carbon-containing raw materials is an important scientific and practical task of great importance for the development of domestic technology of multifunctional zirconium compounds, as well as the effective solution of innovative problems of applied materials science.

2. Theoretical study
Theoretical research includes thermodynamic modeling of plasmosynthesis of zirconium carbide. Thermodynamic modeling of the synthesis processes was carried out with the aim of predicting the optimal conditions for the production of zirconium carbide (ratio of components and temperature), determining the equilibrium process indicators (the degree of conversion of raw materials to carbide,
compositions of gaseous and condensed products), assessing the contribution to the carbide formation of gas-phase reactions that provide plasma conditions technologies for efficient processing of dispersed raw materials [7.8].

The objects of thermodynamic modeling were the C-H-N, Zr-C-H-N and Zr-O-C-H-N systems, which is due to the possibility of using zirconium and its dioxide, hydrocarbon feeds – methane, plasma forming gas – nitrogen as zirconium-containing raw materials. In the calculations, the temperature range 1000–6000 K was considered at a total system pressure of 0.1 MPa. The compositions of gaseous and condensed products necessary for analysis were calculated by the “constant method”. The calculations were performed using the PLASMA computer simulation program for high-temperature complex chemical equilibria, which has an integrated database of interaction products for oxide, boride, carbide, and nitride-forming systems. The ratios of the starting components were set in accordance with the stoichiometry of the reactions of the formation of the target products and the parameters of the processing equipment (plasma gas flow rate).

The simulation results of the raw materials and heat carrier gas interaction for the conditions of a plasma-chemical reactor allow the parameters and implementation indicators of technological options for zirconium carbide production to be predicted. Technological options, parameters and indicators for the production of zirconium carbide are presented in table 1. The calculation took into account the possibility of raw materials loss in the reactor in the amount of 4% and plasma products in the capture system in the amount of 5%.

| Table 1. Predicted parameters and indicators for zirconium carbide production. |
|-------------------------------------------------|-----------------|-----------------|-----------------|
| Technological parameters and indicators          | Option 1 Zr+CH₄+N₂ | Option 2 ZrO₂+CH₄+N₂ | Option 3 ZrCl₄+CH₄+N₂ |
| Consumption of plasma-forming gas (nitrogen), kg/s | 9·10⁻³         | 9·10⁻³         | 9·10⁻³         |
| The initial temperature of the plasma stream, K  | 5400           | 5400           | 5400           |
| Quenching temperature, K                        | 2800           | 2800           | 2800           |
| Mass consumption concentration, kg of raw       | 0.14           | 0.14           | 0.20           |
| materials /kg of nitrogen                       |                |                |                |
| The degree of raw materials conversion to       | 0.96           | 0.96           | 0.96           |
| carbide                                        |                |                |                |
| The carbide yield, %                            | 92.0           | 92.0           | 92.0           |
| Productivity, kg of zirconium carbide /h        | 1.1            | 4.29           | 2.45           |
| The intensity of the process, kg /h²m³          | 647            | 2523           | 1441           |
| Consumption of zirconium-containing raw materials, kg/kg | 2.73           | 0.82           | 2.29           |
| Methane consumption, kg/kg                      | 0.15           | 0.56           | 0.16           |
| Consumption of heat carrier gas (nitrogen), kg/kg | 21.43          | 5.73           | 16             |

3. Pilot study

Subsequently, experimental studies of carbide formation processes occurring in the nitrogen-hydrogen high-temperature flow during plasma processing containing zirconium dioxide – natural gas (methane) were carried out:

1. Based on the results obtained, a zirconium dioxide powder of TsRO grade according to GOST 21907-76, natural gas (methane), and technical nitrogen GOST 9293-84 were selected as raw materials for the production of zirconium carbide. It was established that the product of carbide formation is zirconium carbide ZrC.

2. The equations describing the dependences of the zirconium carbide content and free carbon (in %) in the products on the main technological factors were obtained for the technological option under study:

\[ [\text{ZrC}] = -109.72 + 0.0371 T_0 + 0.0034 T_q - 0.0687 \{\text{CH}_4\}, \]

\[ [\text{ZrO}_2] = 174.44 - 0.02995 T_0 - 0.00236 T_q, \]

\[ [\text{C}_\text{free}] = -101.33 + 0.015 T_0 + 0.0079 T_q + 1.2487 \{\text{CH}_4\} - 0.00019 T_0\{\text{CH}_4\} - 0.00008 T_q\{\text{CH}_4\}, \]

\[ [\text{N}] = -7.092 + 0.0013 T_0 + 0.00064 T_q. \]
(in the equations $T_0$ – the initial temperature of the plasma flow (5000 – 5400 K); $T_q$ – quenching temperature (2000 – 2800 K); $\{\text{CH}_4\}$ – the amount of reducing agent (100 – 130% of the stoichiometrically necessary to obtain ZrC).

3. Peculiarities were determined and a probable mechanism of zirconium carbide formation according to the “vapor-crystal” scheme was proposed, presumably during the interaction of zirconium vapor and cyan. A generalized hypothetical carbide formation scheme has been compiled containing 2 zones: a high-temperature zone (6000 – 3500 K) of formation of the reaction mixture in which the processes of zirconium powder evaporation occur, and a lower-temperature (3500 – 2000 K) in which zirconium vapor is condensed, a significant decrease in hydrocarbons concentration and zirconium carbide formation.

4. A comprehensive physico-chemical certification of zirconium carbide was carried out. It was established that:

- the zirconium carbide content in the obtained products, not in contact with air is 94.2 – 93.61%, related impurities, %: zirconium dioxide 4.56 – 5.27 %, free carbon 1.32 – 1.12 %, nitrogen 1.87 – 2.12%;

- zirconium carbide obtained in the nanocrystalline state, is represented by faceted particles of a cubic shape in the size range from 10 to 40 nm.

Based on the interpretation of the results of theoretical and experimental studies, a continuous technological process for the production of zirconium carbide in the plasma metallurgical reactor was developed.

For the implementation of zirconium carbide plasmosynthesis, a hardware-technological scheme is proposed, shown in figure 1 [9-11], which includes the following operations and stages: 1) input control of raw materials and process gases; 2) preparation of ZrO$_2$ powder: storage, dosing; loading into a powder dispenser; 3) plasma processing; 4) cooling and partial deposition in the quenching and precipitation chamber of the gas stream leaving the reactor to the working temperature of the bag metal fabric filters (600-800 K), separation of zirconium carbide from it in the filters; 5) certification of nanocrystalline ZrC in chemical composition and dispersion, packing in sealed double plastic bags and sending to the warehouse of finished products.

The main quality indicators and technical and economic indicators for zirconium carbide production for the production conditions of custom-made batches are presented in table 2. The production cost and selling price were calculated in accordance with the recommendations [12]. The required investment for organizing the zirconium carbide production in 3 plasma-metallurgical reactors with a total capacity of 450 kW is 123.7 million rubles. At the same time, it is forecasted to achieve an annual output of 54 tonnes/year with a selling price of 35,142 rubles/kg ($ 576 / kg).

The prime cost of zirconium carbide is 20539 rub/kg and has the following structure, %: raw materials, materials, electricity 86; wages and social security contributions 3; maintenance and operation of equipment 4; general shop, general business, commercial expenses 7. The payback period for capital investments is four months.

A comparison of prices with price offers for nanocrystalline zirconium carbide of foreign companies, presented in figure 2, testifies to the competitiveness of the developed technological process.

Based on the interpretation of the results of theoretical and experimental studies, a continuous technological process for producing zirconium carbide in a plasma-metallurgical reactor was developed, including the preparation of raw materials, plasma generation, plasma processing of zirconium-carbon-containing raw materials, the formation of ZrC, its forced cooling and the release of technological gases from the reactor from the stream. The technological process provides, under operating conditions with a coefficient of equipment utilization of 0.7, a productivity of 18.16 tonnes/year per reactor at a selling price of 35142 rubles/kg.
Figure 1. Process flow diagram for zirconium carbide production: 1 – rubbing of the powdered raw materials; 2 – loading of ZrO₂ powder into the dispenser; 3 – plasma treatment; 4-5 – cooling of the exhaust dust and gas flow and separation of the target product; 6 – collection, quality control and packaging; 7 – absorption option of exhaust gases neutralization.

Technical forecasts and suggestions for zirconium carbide use as part of functional protective coatings formulated on the basis of the formed ideas about its physicochemical properties features in the nanocrystalline state. In the conditions of Polimet LLC, the expediency of using zirconium carbide in the composition of corrosion-resistant protective coatings based on nickel instead of the used nanodiamonds was established.

Table 2. Key quality indicators and technical and economic indicators of zirconium carbide production.

| Indicators                                      | Value       |
|------------------------------------------------|-------------|
| Production area, m²                            | 300         |
| Installed power, kW                            | 450         |
| Number of reactors, pcs                        | 3           |
| Equipment utilization ratio, the share of units| 0.7         |
| Schedule, number of shifts                     | 2 shifts x 12 hours |
| Investments in fixed and current assets, mln. rub. | 123.7      |
| The specific gas flow rate of the coolant (nitrogen), t/t | 5.73       |
| Specific consumption of natural gas (methane), t/t | 0.15       |
| Specific consumption of zirconium-containing raw materials, t/t | 0.99       |
| Specific energy consumption, thousand kW·h/t  | 42.81       |
| The content of the main phase (ZrC), %        | 92          |
| Annual need for raw materials, t/year         | 26.3        |
| - zirconium dioxide ZrO GOST 21907-76         | 4.9         |
| - природный газ (метан) - natural gas (methane) |            |
| Annual productivity, t/year                   | 54.5        |
| Planned cost, rub/kg                          | 20539       |
| Price (as of 05/01/2018), rub/kg               | 35142       |
| Payback period for capital investments, years | 0.3         |
Figure 2. Global price level for nanocrystalline zirconium carbide: 1 – proposed technology; 2–“American Elements” (Los Angeles); 3 – “PlasmaChem GmbH” (Berlin); 4 – “NEOMAT Co” (Salaspils); 5 – “Nanostructured & Amorphous Materials, Inc.” (Houston).

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