Peculiarities of Production of Chromium Carbonitride Nanopowder and Its Physical-Chemical Certification

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Abstract. Scientific and technological basics of plasma synthesis of chromium carbonitride have been developed, including analysis of the current production state and application of chromium carbon compounds, defining characteristics of three-jet plasma reactor, modeling-mathematical study of interaction of raw materials and plasma streams, prediction of technological parameters of plasma stream based on the modeling results, selection of optimal technological option, implementation of plasma-metallurgical technology of chromium nitride production, its physical-chemical certification and defining technical-economical production factors.

Introduction
Carbide Cr3C2 that is close in composition and structure to chromium-carbonitride Cr3(C0.80N0.20)2 is wear- and corrosion-resistant, hard, chemically-inert material which is in demand in modern engineering and technologies for manufacturing protective coatings of metals and cermets, and as components and alloy additives of tungsten-free hard alloys. Analyzing current state of national and world production and application of chromium carbide three groups of its production methods can be distinguished (regarding aggregative state of raw materials and main application areas): (i) carbothermal reduction of chromium oxide in powder or compact form in non-oxidizing atmosphere (N2, H2, vacuum, inert gas); (ii) carbothermal reduction of chromium oxide in molten metal; (iii) carbothermal reduction of chromium oxide in gas phase. Chromium carbide obtained by the first group of methods is applied in powder metallurgy in cermet technology, the second is used for sputtering and welding deposition of protective coatings, the third one is used in nanomaterials. Further perspectives of chromium carbide application are associated with its production in nanostate. Technology of plasma metallurgical synthesis refers to the third group of chromium carbide obtaining methods. It was developed and utilized in 80-s within integrated scientific and technical program of national scale “Siberia” headed by M.F. Zhukov, academician of the Russian Academy of Sciences and Professor G.V. Galevsky. Technology implies using three-jet direct-flow plasma reactor (with power up to 50 kW) and nitrogen as plasma-forming gas. Implementation of the suggested plasma-metallurgical technology is environmentally-friendly, providing obtaining of chromium nanocarbide close in composition to stoichiometric, presented as nanopowders with particles size 30–70 µm. It also makes possible to separate nanodispersed pyrolytic carbon and product of hydrogen cyanide collecting – technical sodium cyanide. Along with benefits this technology also has disadvantage, i.e. technical and economical inexpedience of using propane-butane mix as carbidizer as it requires for processing...
nitrogen-ammonium-hydrogen plasma which is complex in its composition and difficult to generate. It is also hard to generate this process in laboratory conditions.

The present work is aimed at developing scientific and technological basics of plasma synthesis of chromium carbonitride and its physic-chemical certification.

**Experimental methodology**

Siberian State Industrial University has significant experience in research and running of three-jet direct-flow plasma reactor with nitrogen-based arc plasma jets and its application for synthesis of hard-melting carbides, borides and their composites. The optimum plasma reactor structure is to have uniform placement of plasma jets along the periphery, with angle of slope of plasma streams to the reactor axis 30–45º and heat protection of intensively cooled walls, providing optimal operation mode of mixing chamber, high uniformity of radial temperature distribution and velocity while providing minimum heat losses. However these results are obtained for laboratory plasma reactor (power up to 30-50 kW). The results lack design and technological proposals and recommendations on its industrialization. There also lacks complete information on its thermal and technological characteristics.

Thermo-technical study has been carried out to define industrial power level of three-jet reactor (power range 80-250 kW). The study included determining heat efficiency of plasma jets, specific enthalpy of plasma flow at the reactor input, mass flow rate of plasma-forming gas which is generated in these conditions. It was established that reactor power of 150 kW corresponded to a combination of heat efficiency, required enthalpy of plasma-forming gas and its mass flow rate close to optimal. Further increase in power level is inappropriate since the required enthalpy of plasma flow is not provided within the available plasma jets options. For a three-jet reactor with internal channel diameter of 0.054 m and power 150 kW, the mean mass temperature of plasma flow at length 12 calibres varies within (5500 ±2650) K for an unlined channel and (5500 ±3200) K while its thermal insulation with zirconium dioxide cylinder (0.005 m thick). At the same time the internal surface temperature varies in the range of (800 ±350) K and (1900 ±850) K correspondingly. Specific electric power reaches 1214 MW/m³, significantly exceeding this value for traditional electro-thermal equipment (generally about 0.2 MW/m³). The calculated working life of electrodes for copper anode is 4700 h and 111 h for tungsten cathode. Predicted contamination of chromium carbide with erosion products does not exceed 0.0001 % of copper and 0.00002 % of tungsten. Considering all the characteristics three-jet plasma reactor (power 150 kW) can be referred to high-efficient and reliably operating electro-thermal equipment [1].

Modeling-mathematical study of raw materials and plasma flows interaction included carrying out thermo-dynamic and kinetic analysis. Due to use of chromium, oxide Cr₂O₃ and trichloride CrCl₃, hydrocarbon (methane) and plasma-forming gas (nitrogen) in synthesis as chromium-containing raw materials, systems under study were considered as C–H–N, Cr–O–C–H–N, Cr–Cl–C–H–N, Cr–C–H–N.

Thermo-dynamic analysis of synthesis processes was carried out in order to predict optimum parameters of chromium carbide production (correlation of components and temperature); to determine characteristics of the process (degree of conversion of raw materials into carbide, compositions of gaseous and condensed products) for quasi-equilibrium conditions in the absence of condensed carbon; and to assess the input of gas-phase reactions into carbide-formation processes, providing effective processing of dispersed raw materials in plasma processes. Compositions of gaseous and condensed products necessary for the analysis were calculated by “constant” method which is based on joint solution of the following equations: law of mass action, material-balance equation, and equation for the total number of gas mixture moles, equation for existence of condensed phase and Dalton law. Equations were solved by means of software program for modeling of high-temperature complex chemical equilibrium “PLASMA” (Institute of Solid State and Mechanical Chemistry, Siberian Branch, the Russian Academy of Sciences), with embedded database of
interaction products for oxide-, boride-, carbide- and nitride- forming systems [2]. Temperature range considered in calculations: 1000-6000 K, total pressure in the system: 0.1 MPa.

Multivariant modeling-mathematical study of macro-kinetic parameters of dispersed chromium-containing raw materials evaporation was carried out using modified mathematical modeling of interaction between plasma and raw materials flows of A.L. Mosse – I.S. Burov – G.V. Galevsky, based on a joint solution of equation of raw particles motion, equation of inter-component heat transfer and heat transfer of plasma flow with reactor walls. It also takes into consideration influence on the intensiveness of heat transfer of dispersed raw materials and artificial thermal insulation of channel [2].

Technological studies was carried out in NPF Polimet plant on the base of industrial plasma-technological complex (power 150 kW), including three-jet direct-flow plasma reactor, systems of electricity-, gas- and water-supply, batching of burden materials and catching of synthesis products.

Three electric arc heaters (plasma jet) EDP-104A (power up to 50 kW) are used to generate plasma flow in reactor. They are placed in mixing chamber under angle 30 ° to the reactor axis.

Mixing chamber is connected with sectional water-cooled channel with internal diameter of 0.064 m. In order to reduce radial temperature gradient in near-wall zone, reactor is lined with cylindrical insertions of zirconium dioxide (wall thickness 0.005 m), outer diameter of 0.064 m, that decreases the diameter of its channel up to 0.054 m. Alteration of reactor length and supply of cold gas (nitrogen) into plasma flow through hardening ring (placed at the output from reactor) enable to perform hardening of synthesis products in different temperature zones. Supply of high-dispersed raw materials into mixing chamber is performed by means of water-cooled lance.

Electric power supply of industrial plasma jet is made by thyristor of series ATP-750/600. Batch meter of combined electro-mechanical and gas-vortex type with demountable cylinder – receiver of powder raw-materials is used for batching. Catching system of synthesis products includes collection chamber, collecting around 10 % of nanopowder where process gas temperature reduces up to 873 K, and two filter bags working by turn, collecting up to 85 % of nanopowders.

Nitrogen of technical purity was used as plasma-forming gas (oxygen content up to 0.5 % vol.), metal chromium PK-1M (tech. spec. 14-1-1474-75, updat.) was used as chromium-containing raw material, natural gas with methane content up to 94 % vol. (the rest is ethane, propane, butane).

Technological studies allowed finding dependence of chromium carbonitride content (close in composition to carbide) and corresponding admixtures in synthesis products on the defining factors, presented as following equations:

\[
[\text{Cr}_3(\text{C}_{0.8}\text{N}_{0.2})_2] = 66.12 + 0.03T_0 - 0.42C_{\text{H}_2} - 0.14C_{\text{NH}_3} - 0.00002T_3C_{\text{NH}_3} \quad (1)
\]

\[
[\text{Cr}_{\text{free}}] = 147.95 - 0.027T_0 - 0.34C_{\text{H}_2} - 1.37C_{\text{NH}_3} + 0.0003T_0C_{\text{NH}_3} \quad (2)
\]

\[
[\text{C}_{\text{free}}] = -150.30 - 0.002T_0 + 1.3C_{\text{H}_2} + 13.5C_{\text{NH}_3} - 0.00008T_0C_{\text{NH}_3} + 0.0002T_3C_{\text{H}_2} \quad (3)
\]

\[
[\text{Cr}_2\text{O}_3] = 41.80 - 0.0069T_0 - 0.208C_{\text{CH}_4} + 0.00004T_0C_{\text{CH}_4} \quad (4)
\]

\[
[\text{N}_{\text{comb.}}] = 1.74 + 0.001T_0 - 0.012C_{\text{H}_2} - 0.03C_{\text{NH}_3} - 0.00001T_3C_{\text{NH}_3} \quad , \quad (5)
\]

where \([\text{Cr}_3(\text{C}_{0.8}\text{N}_{0.2})_2] \), \([\text{Cr}_{\text{free}}] \), \([\text{C}_{\text{free}}] \), \([\text{Cr}_2\text{O}_3] \), \([\text{N}_{\text{comb.}}] \) – content, in % wt, of carbonitride, free chromium and carbon, chromium oxide (III) and combined nitrogen in synthesis products; \(T_0 \) and \(T_3 \) – initial temperature of plasma flow and hardening temperature, \(K \); \(C_{\text{CH}_4} \) – amount of hydrocarbon from stoichiometrically necessary for chromium carbidization, %; \(C_{\text{H}_2} \) – hydrogen concentration in plasma-forming gas, % vol.; \(C_{\text{NH}_3} \) – amount of atomic nitrogen in plasma-forming gas, \(N (\text{NH}_3) / C (\text{CH}_4) \), % from stoichiometric.

The average size of chromium nanocarbide particles formed in plasma flow, calculated by the value of specific surface is proportional to mean mass temperature of flow in degree -2.96 (equation 6):
\[ \bar{d} = (726 \pm 35,1) \times 10^{(-2,96 \pm 0,436)} \]  

(6)

Complex physico-chemical certification of synthesis products by means of X-ray and chemical analysis requires study of crystal lattice and phase and chemical composition. Dispersiveness and particles morphology was studied by transmission electron microscopy and scanning electron microscopy (SEM). Similar approach for synthesis products identification is described in works [3-5].

**Results and discussion**

Results of thermo-dynamic modeling of high-temperature interaction in chromium-carbon-containing systems are given in Fig. 1-3. Thermal-dynamic analysis of the selected technological options showed that in systems Cr:O:C:H:N and Cr:C:H:N 100 % output of chromium carbide was possible by stoichiometric ratio Cr:C and C:H and temperature 2000–2200 K. In the system Cr–C–Cl–H–N 100% output of chromium carbide is reached by stoichiometric ratio Cr:C, 3-fold excess amount of hydrogen and temperature 2000-2200 K. Formation of chromium carbide occurs with condensed chromium and hydrogen cyanide according to mechanism “vapour – molten metal – crystal” thus enabling to suppose that it can reach high output in real synthesis conditions.

![Thermo-dynamic calculations](image)

a) equilibrium compositions of gas and condensed phases depending on the temperature at ratio Cr:O:C:H:N = 0,25:0,375: 0,375:1,5:20

b) quasi-equilibrium compositions of gas and condensed phases depending on the temperature at ratio Cr:O:C:H:N = 0,25:0,375: 0,54:2,16:20

Figure 1. Results of thermo-dynamic calculations of system Cr:O:C:H:N
a) quasi-equilibrium compositions of gas and condensed phases depending on the temperature at ratio Cr:C:H:N = 0,25:0,16: 0,64:20

b) dependence of degree of conversion Cr in Cr,C2 of the ratio Cr:C = 0,25:0,042 (1); 0,25:0,082 (2); 0,25:0,116 (3); 0,25:0,125 (4); 0,25: 0,145 (5); 0,25:0,16 (6)

Figure 2. Results of thermo-dynamic calculations of system Cr:C:H:N

Figure 3. Quasi-equilibrium compositions of gas and condensed phases of system Cr–C–Cl–H–N at components ratio Cr:C:Cl:H:N = 0,25:0,16:0,75:2,0:20

The degree of raw materials evaporation is calculated for interaction of dispersed chromium-containing raw materials with highly heated gas flow in plasma jet depending on the energy parameters of reactor, fineness, speed of input into plasma flow and mass-expendable concentration. With power 75 kW, 100 % evaporation degree for chromium particles with fineness 10…30 µm while mass-expendable concentration 0,14…0,12 kg of chromium powder / kg of exchange gas. For chromium oxide (III) and chromium chloride (III) these values comprise 5…20 µm and 0,14…0,10 kg/kg, 30…70 µm and 0,16…0,14 kg/kg correspondingly. Based on the obtained results raw materials for chromium carbide synthesis were selected.

Results of modeling-mathematical study enabled to predict technological parameters of plasma-metallurgical production of chromium carbide for different types of chromium-containing raw materials and to select optimal technological option (Table 1).
Table 1. Predicted technological parameters of plasma-metallurgical production of chromium carbide

| Process variables                                | Carbidization of chromium with methane | Recovery of Cr$_2$O$_3$ with methane | Recovery of CrCl$_3$ with methane |
|--------------------------------------------------|---------------------------------------|--------------------------------------|----------------------------------|
| Degree of conversion of raw materials            | 0.95                                  | 0.95                                 | 0.95                             |
| Output of chromium carbide, %                    | 92.0                                  | 90.0                                 | 91.8                             |
| Production capacity of chromium carbide, kg/h    | 3.42                                  | 2.79                                 | 1.69                             |
| Production intensity, kg/h·m$^3$                 | 1368                                  | 1116                                 | 676                              |
| Chromium-containing raw materials consumption, kg/kg | 0.9                                  | 1.3                                  | 2.76                             |
| Consumption of exchange gas, kg/kg               | 9.47                                  | 11.6                                 | 19.7                             |
| Methane consumption, kg/kg                       | 0.175                                 | 0.58                                 | 0.18                             |
| Electrical energy consumption, kW·h /kg          | 65.79                                 | 80.65                                | 133.14                           |

While calculating the variables, losses of raw materials in reactor were considered as 4 % and losses of synthesis products in catching system were considered in the amount of 5 %. It can be seen that optimal technological option is chromium carbidization with natural gas.

Optimal values of technological factors and acceptable limits of their alteration, as well as basic characteristics of synthesized by these conditions chromium carbonitride are given in Table 2 (five-fold repetition of experiments).

Table 2. Acceptable limits in alteration of parameters of chromium carbonitride synthesis in industrial reactor (power 150 kW) and its main characteristics

| Synthesis parameters and characteristics of chromium carbonitride | Value |
|------------------------------------------------------------------|-------|
| Composition of exchange gas, % vol. – nitrogen                   | 100   |
| Composition of carbidizer, % vol.                                 |       |
| – methane                                                        | 93.6  |
| – ethane                                                         | 3.0   |
| – propane                                                        | 2.2   |
| – butane                                                         | 1.2   |
| Composition of chromium-containing raw materials, % wt.          |       |
| – metal chromium                                                 | 99.3  |
| Fineness of chromium-containing raw materials, µm                | –10   |
| Production capacity of raw materials, kg/h                       | 3.11  |
| Amount of carbidizer, % from stoichiometric                      | 120–140|
| Initial temperature of plasma flow, K                           | н.м. 5400|
| Hardening temperature, K                                         | 2000–2200|
| Phase composition                                                |       |
| Chemical composition, % wt.                                      |       |
| – Cr$_3$(C$_{0.80}$N$_{0.20}$)$_2$                               | 91.8–93.45|
| – free chromium                                                  | 2.10–1.80|
| – free carbon                                                    | 1.30–1.10|
| – chromium oxide (III)*                                          | 4.00–3.00|
| – volatiles                                                      | 0.80–0.60|
Synthesis parameters and characteristics of chromium carbonitride

| Parameter                                      | Value       |
|------------------------------------------------|-------------|
| Output of chromium carbonitride, % wt         | 92.0        |
| Specific surface, m²/kg                       | 32000–37000 |
| Size of particles, µm                         | 30–35       |
| Particles shape                               | spherical   |
| Degree of oxidation chromium carbonitride nanopowder x10^7, kg O₂/m² | 2.56        |
| Production capacity, kg/h                     | 3.42        |
| Production intensity, kg/h·m³                 | 1368        |

Note: * defined by oxygen content;  
** calculated by value of specific surface;  
*** defined after exposure on air during 24 hours

Resulting from integrated physical-chemical certification of synthesis products it was established that product of plasma synthesis is ternary compound – chromium carbonitride. X-ray diagram Cr₃(C₀.₈ₐN₀.₂₀)₂ is given in Figure 4.

![Figure 4. Fragment of X-ray diffractogram of chromium carbonitride](image)

Cr₃(C₀.₈ₐN₀.₂₀)₂, is identified as rhomb-shaped carbonitride with crystal structure which differs from carbide structure by presence of octahedral structural elements, nitrogen atoms being placed inside them. Within the studied range of synthesis parameters alteration, chromium carbonitride composition is almost not changed and within limit of accuracy of analysis and calculation it corresponds to Cr₃(C₀.₈ₐN₀.₂₀)₂. Content of chromium nanocarbonitride in synthesis products makes 91.8 – 93.5 % wt. Microphotographs of chromium nanocarbonitride are given in Fig. 5.

![Figure 5. Microphotographs of chromium nanocarbonitride – SEM](image)

a – layout; b – morphological pattern of aggregate; c – ensemble of particles and aggregates; d – separate particles
Nanopowder of chromium carbonitride is presented as aggregates of spherical or close to that form, size from 600 to 150 µm, formed by association of globular particles of quite broad size range – from 20 to 80 µm, their number in aggregate depends on its fineness. Nanolevel and morphology of particles allow considering them as products of carbonization of chromium microdroplets, formed while volume condensation of its vapors, liquid drop coalescence and crystallization. Presence of aggregates of different volume in the studied objects demonstrates high probability of further coarsening of nanoparticles at temperature fall by means of their coagulation.

Evaluation of the economical efficiency of plasma-metallurgical production of chromium carbonitride shows that while production output 3.7 t of chromium carbonitride per year (calculating per one reactor) and production cost 47 $/t retail price is 220 $/kg, that testifies its competitiveness on a world market of nanopowder materials. Currently leading foreign producers of carbide nanopowders, including scientific-industrial “Nanostructured & Amorphous Materials. Inc.” (USA); “Tokyo Tekko Co” (Japan); “Hefei Nanotechnology & Development htd. Co” (China); “Neomat Co” (Latvia); “Plasma Chem Gmbh” (Germany) set the price range for carbides nanopowders within 400–2000 $/kg. Payback period on investments is 1.5 year, thus proving economical and technological expedience of chromium carbonitride production. One of the most preferable application areas of chromium carbonitride is technology of composite electro-deposition of protective coatings, as well as some materials, as described in [6-10].

Conclusions

Based on the conducted modeling-mathematical and technological studies optimal values for synthesis parameters of chromium nanocarbide and its physical-chemical parameters were defined. It is established that while carbidization of chromium powder with methane in conditions of nitrogen plasma flow in temperature range 5400 – 2000 K chromium carbonitride Cr3(C0.8N0.2)2 is formed. Phase and chemical compositions were studied, as well as dispersiveness, morphology and degree of oxidation of synthesis products. The main technical-economical parameters of the suggested technology have been defined, such as production capacity, production intensity, production cost and retail cost.

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