Development and application of a complex model of titanium diboride plasmosynthesis

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Abstract. An integrated multifactor mathematical model of plasmosynthesis of titanium diboride was developed. The model includes 3 submodels: “Plasma generation”, “Evaporation of raw materials”, “Boride formation”. The model provides the implementation of multivariate research and engineering calculations of plasma processing technological indicators of various types of titanium-containing raw materials, industrial products and waste. The convergence of the predicted and practical results for various types of raw materials is 10.4-12.9%. In all cases, lower values of practical data are noted in comparison with the calculated ones, which is due to the influence of non-isothermal heat carrier gas.

1. Introduction

To solve design and technological problems and perform multivariate research and engineering calculations of effective plasma metallurgical processing of various types of titanium-containing raw materials, industrial products and waste, a complex model of boride formation has been developed.

The classical approach to construction of complex multifactorial deterministic model of a complex metallurgical process involves dividing it into component subprocesses and formation of the corresponding submodels based on the joint solution of the systems of mathematical equations describing them [1]. Given that the solution of the equations is carried out under the inevitability of a number of assumptions, the simulation results are predictive. Nevertheless, for the study of metallurgical processes, mathematical modeling is widespread enough, since with the appropriate computer software it allows for multivariate calculations and ensures the accumulation of information important for technological design.

2. Development of an integrated model

For the correct construction of a complex model, it is necessary to correctly pose the problems that are solved within the framework of each submodel in terms of their physical and chemical nature. Of the 7 components of plasma processing of the powder mixture of sequentially implemented technological processes (stages), three stages are the main ones that determine the quality of diboride as a commercial product. This is 1) generation of a high-enthalpy gas flow; 2) mixing powdered raw materials with plasma, its heating and evaporation; 3) the formation of a reaction boride-forming mixture, the formation of TiB₂ and the formation of its nanoparticles as a result of coalescence and coagulation processes. This determines the possibility of constructing a model based on three submodels: “Plasma generation” (1); “Evaporation of raw materials” (2); “Boride formation” (3).
Submodel 1 “Plasma generation” is based on the use of the following calculated dependences of the thermal and gas-dynamic characteristics of the plasma jets generated in plasmatrons and the plasma flow formed in the mixing chamber of the reactor:

\[
\eta_n = [1 + 5.85 \cdot 10^{-5} \left( \frac{l^2}{G_g d_1} \right)^{0.27} \left( \frac{G_g}{d_1} \right)^{-0.27} (P_{N_2} \cdot d_1)^{0.3} \cdot \left( \frac{l_1}{d_1} + \frac{l_2}{d_2} \right)^{0.5}] \]

\[
U = \frac{11044}{10^{0.03M}} \left( \frac{G_g}{d_1} \right)^{3} \]

\[
\frac{H_c}{G_g} = \frac{N_n \eta_n}{G_g} \]

\[
T_c = f(H_c) \]

\[
Re_c = \frac{\mu_c}{\rho_c} \]

\[
N = 3 \cdot P \cdot \eta_n \cdot \eta_m \cdot \eta_c \]

\[
H_n = \frac{N}{3d_g} \]

\[
T_n = f(H_n) \]

\[
Re_n = \frac{v_n d_s \rho_n}{\mu_n} \]

The following notation is used in equations (1-9): \(N_n\) is the given power of the plasma torch, kW; \(U\) is the voltage across the arc, \(V\); \(I\) – arc current, A; \(M\) is the molecular weight of nitrogen; \(G_g\) is the mass flow rate of the plasma-forming gas in the plasmatron, kg/s; \(d_1\) and \(l_1\) – diameter and length of the arc channel of the plasma torch, m; \(d_2\) and \(l_2\) – diameter and length of the ledge of the plasma torch, m; \(P_{N_2}\) – nitrogen pressure at the exit of the plasma torch, Pa; \(H^5\) and \(H_6\) are the specific enthalpy of the plasma jet and plasma flow, respectively, at the exit from the anode of the plasma torch and at the entrance to the reactor channel, kJ/kg; \(T_c\) and \(T_n\) are the mass-average temperature of the plasma jet and plasma stream, respectively, at the exit from the anode of the plasma torch and at the entrance to the channel of the reactor, K; \(\eta_n, \eta_m, \eta_c\) – thermal efficiency of the plasma torch and mixing chamber, fractions of a unit; \(N\) is the net power supplied to the reactor, kW; \(Re_c, Re_n\) – Reynolds numbers determined for the conditions of the expiration of the plasma jet from the anode and the entry of the plasma flow into the reactor channel; \(v_c, \rho_c, \mu_c\) – velocity, density and viscosity of the plasma jet at the temperature \(T_c\) respectively m/s, kg/m³, Pa s; \(v_n, \rho_n, \mu_n\) – are the velocity, density and viscosity of the plasma flow at a temperature \(T_n\), respectively, m/s, kg/m³, Pa s.

Equations (1, 2) were obtained by the scientific school of academician M.F. Zhukov [2] for the plasma-powered plasma torch EDP-104A based on the processing of experimental data using the theory of similarity. The submodel predicts the thermal and gas-dynamic characteristics of the plasma jets formed in the plasma torches and the plasma formed in the mixing chamber upon their collision, depending on the flow rate of the plasma-forming gas and the power supplied to the plasma torches.

Submodel 2 “Evaporation of raw materials” was proposed by A.L. Mosse and I.S. Burov [3] and is based on the joint solution of the equations of motion of raw materials, inter-component heat transfer and heat transfer of the plasma stream with the walls of the reactor, provides prediction of energy regimes of effective processing of various titanium-boron-containing raw materials. In this case, the dependence of the degree of evaporation \(K_p\) on the characteristics of the raw material (density \(\rho_p\), specific heat \(C_p\), thermal conductivity coefficient \(\lambda_p\), temperatures of initial \(T_0\), melting \(T_{pm}\), evaporation \(T_{pn}\), heat of fusion \(\Delta H_m\) and evaporation \(\Delta H_n\), particle diameter \(d_p\) and particle shape coefficient \(\mu_s\) and parameters of the reactor operation and the process (power supplied to reactor \(N\), mass flow rate of plasma-forming \(G_g\) and transporting gas \(G_t\), raw materials \(\mu_s\), diameters of the channels of the reactor \(D\) and lance \(D_0\)) are taken into account

\[
K_p = f(\rho_p, C_p, \lambda_p, T_{pm}, T_{pn}, \Delta H_m, \Delta H_n, d_p, f_p, G_g, G_t, \mu_s, D, D_0) \]
Submodel 3 “Boride formation” should be based on equations that take into account the influence of kinetic factors on the yield (content in products) of titanium diboride and equations describing the evolution of the dispersion of its particles in a plasma stream.

Kinetic equations should be formulated for the most likely boride formation reactions. However, the use of high-temperature kinetic calculations for processes involving the condensed phase in atmospheric pressure plasma using classical chemical kinetics methods is difficult due to the lack of information on the most likely boride formation reactions and the complete absence of data on their rate constants for the temperature range under study. In this regard, the macrokinetic approach seems to be more real, suggesting the choice of equations of the form obtained in [4] for the submodel

\[
[TiB_2], [Ti_{free}], [B_{free}], [C], [TiO_2] = f(K_p, T_0, T_3, \{H_2\}, \{B\}, \{CH_4\})
\] (11)

The equations describe the dependence of the titanium diboride content in plasma products on the degree of evaporation of the feed \(K_p\), initial temperature \(T_0\), quenching temperature \(T_3\), the amount of boron in the charge \(\{B\}\), the hydrogen concentration in the plasma gas \(\{H_2\}\), and the amount of the reducing agent \(\{CH_4\}\) for TiO\(_2\). The results obtained in studying the features of the boride formation process under the conditions of a plasma flow indicate a high probability of TiB\(_2\) formation during crystallization of a titanium-boron-containing melt – a product of boriding by boron hydride of metal aerosol formed during the volume condensation of titanium vapor. This predetermines at least a two-stage review of this complex process.

However, the analysis of specialized scientific and technical literature indicates that a universal comprehensive model of the condensation process has not yet been developed, although theoretical options for predicting the dispersion of solid particles of condensation origin have been proposed.

The aforementioned and yet insurmountable shortcomings of the known mathematical models of the formation of nanoparticles under the conditions of a plasma flow prompted a number of researchers to study experimentally the temperature dependence of the average particle size during their enlargement [10-17].

The dependence obtained by the authors [17] for the synthesis in the plasma stream of TiB\(_2\) from the reaction mixture (TiO\(_2\)+B+C\(_3\)H\(_6\)+C\(_4\)H\(_10\)) and the temperature range 2500–3200 K has the following form (\(d\) in m, \(T\) in K)

\[
d = (1.46\pm0.025)\cdot10^{-5}\cdot T^{-0.741\pm0.165}
\] (12)

This temperature dependence is accepted as a calculated one for describing the evolution of the dispersion of TiB\(_2\).

The structure of the mathematical model of boride formation processes is shown in figure 1. To simulate the boride formation process, a computer program “Modeling of the plasma synthesis of titanium boride” was created, which represents a complete product with the possibility of implementation on IBMPC computers running MS Windows and installed Microsoft Accesses. The program is registered in the joint fund of electronic resources “Science and Education” of the Russian Academy of Education (certificate on registration of electronic resource No. 21506 dated 12/07/2015).

3. Application of the model
Using the developed mathematical model, the parameters of plasma jets and flow, the conditions for the efficient evaporation of powdery raw materials and boride formation, and the dispersion evolution of boride nanoparticles, the results of which are presented in figures 2–6, were calculated. It can be seen that the efficiency of boride formation processes is directly determined by the conditions of evaporation of the raw material, boron gasification and methane pyrolysis.

4. Assessment of model adequacy
The accuracy of the developed model was evaluated by two methods:
for option 1 (Ti+B+H₂) using a test sample obtained by processing in a plasma reactor a mixture containing PTM grade titanium powder with a grain size of 40 μm;

- for option 2 (TiO₂+CH₄+B+H₂) by comparing the calculated degree of evaporation of TiO₂ and the experimentally determined degree of its reduction in the conditions of a plasma flow; the degree of recovery was determined by the ratio of the actual and equilibrium concentration of carbon monoxide in the process gases.

The accuracy assessment results for option 1 are shown in table 1, for option 2 in table 2. They confirm sufficient convergence of the predicted and practical results. In all cases, lower values of practical data are noted in comparison with the calculated ones, which is apparently caused by the influence of nonisothermal gas flow – the heat carrier.
Figure 3. The dependence of specific enthalpy (a), mass average temperature (b) and Reynolds number (c) of the plasma flow at the inlet of the reactor channel on its power
\(G_0 = 3 \times 10^{-3} \text{ kg/s}, D = 0.054 \text{ m}).

(a) \(\mu_p = 0.14 \text{ kg/kg}, T_p = 5400 \text{ K}, T_3 = 2800 \text{ K}, [\text{B}] = 112.5 \%, \{\text{H}_2\} = 10 \% \text{ vol.};
(b) \(d_p = 5 \text{ \mu m}, T_p = 5400 \text{ K}, T_3 = 2800 \text{ K}, [\text{B}] = 112.5 \%, \{\text{H}_2\} = 10 \% \text{ vol.};
(c) \(d_p = 5 \text{ \mu m}, \mu_p = 0.14 \text{ kg/kg}, T_p = 5400 \text{ K}, T_3 = 2800 \text{ K}, \{\text{H}_2\} = 10 \% \text{ vol.}

Figure 4. The dependence of the content (a) of titanium diboride in plasma products on the fineness of titanium powder (a), its mass consumption concentration (b) and the boron content in the charge (c) (Option 1 – (Ti+B+H\(_2\))).

Figure 5. The dependence of the content of (a) titanium diboride in plasma products on the fineness of titanium powder (a), its mass consumption concentration (b) and methane consumption (c) (Option 2 – (TiO\(_2\)+CH\(_4\)+B+H\(_2\))).
Figure 6. Evolution of the dispersion of titanium diboride nanoparticles in the plasma flow.

| Table 1. Comparison of calculated and experimental results for option 1. |
|-----------------------------|-----------------------------|-----------------------------|
| $T_0$, K | $y_{calc}$ | $y^1_\varepsilon$ | $y^2_\varepsilon$ | $y^3_\varepsilon$ | $y^4_\varepsilon$ | $y^5_\varepsilon$ | $y_{av\varepsilon}$ | Deviation, % |
| 5400 | 36.6 | 34.9 | 32.1 | 31.2 | 30.5 | 30.9 | 31.9 | 12.9 |
| 5000 | 24.3 | 21.3 | 20.9 | 19.4 | 22.2 | 21.5 | 21.1 | 12.8 |

| Table 2. Comparison of calculated and experimental results for option 2. |
|-----------------------------|-----------------------------|-----------------------------|
| $T_0$, K | Evaporation rate, % | Degree of reduction $\alpha$, % | Deviation, % |
| | | $\alpha^1_\varepsilon$ | $\alpha^2_\varepsilon$ | $\alpha^3_\varepsilon$ | $\alpha^4_\varepsilon$ | $\alpha_{av\varepsilon}$ | |
| 5400 | 100.0 | 88.1 | 90.9 | 89.8 | 89.6 | 10.4 |
| 5000 | 82.0 | 71.3 | 70.2 | 73.6 | 71.7 | 12.6 |

5. Conclusion

An integrated multifactor mathematical model of boride formation processes, that occur during the plasma metallurgical processing of titanium-boron-containing raw materials, was developed, including 3 submodels: 1) “Plasma generation”, 2) “Evaporation of raw materials”, 3) “Boride formation”. The model has a block structure and allows the parameters of plasma jets and flow, conditions for efficient evaporation of powdery raw materials and boride formation, the evolution of the dispersion of boride nanoparticles to be calculated. A computer program was created for submodel 3 “Boride formation” (Certificate No. 21509 on registration in the joint fund of electronic resources “Science and Education” of the Russian Academy of Education). The effectiveness of the use of a complex mathematical model for performing research and engineering calculations of plasma processing technological indicators of various types of titanium-containing raw materials was confirmed.

References

[1] Tsymbal V P 2006 Mathematical Mmmodeling of Complex Systems in Metallurgy: a Textbook for Universities (Kemerovo, Moscow: Kuzbassvuzizdat) p 431
[2] Zhukov M F et al 1995 Plasmatrons. Research. Problems (Novosibirsk: SB RAS) p 203
[3] Krasovskaya L I and Mosse A L 2000 Plasma-chemical Processes in Three-jet Electric Arc Reactors (Minsk: Institute of Heat and Mass Transfer n.a. A V Lykov of NAS of Belarus) p 196
[4] Galevsky G V, Efimova K A and Rudneva V V 2015 Scientific and Technical Journal of SPhSPU 2(219) 141–150
[5] Solonenko O P et al 1995 Thermal Plasma and New Materials Technology: In 2 Volumes vol 2 (Cambridge: Cambridge Intersci) p 533
[6] Solonenko O P, Polak L S et al 1995 Thermal Plasma Investigations and Design of Thermal Plasma Technologies vol 2 (Cambridge: Cambridge Intersci) p 533