Thermodynamic Estimation of the Parameters for the C–H–O–N–Me-Systems as Operating Fluid Simulants for New Processes of Powder Thermal Spraying and Spheroidizing

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Abstract. Over the past few years, a group of new processes was developed for high-temperature, including plasma electric arc spraying (at ambient pressure) and spheroidizing of some ceramic and metal powder materials with the use of gaseous hydrocarbons in the heat carrier as well as with feeding of organic additions into a high-temperature jet, in particular, polymeric ones, to control porosity of sprayed metallic functional coatings. The paper considers the possibility to modify such technological processes by introducing solid fuel additions of a polymer type into the operating fluid of an apparatus for gas-thermal (plasma or other) treatment, which provides melting of metal or oxide powders. For this, with the help of thermodynamic analysis, the processes have been evaluated at temperatures (300–3000) K for the set of such reacting five component systems as C–H–O–N–Me (at ambient pressure 0.101 MPa) with five variants of Me – aluminum, titanium, chrome, copper, nickel. This makes it possible to consider these systems as simulants for potential technologies for the treatment of oxide powders (Al₂O₃, TiO₂, Cr₂O₃) as well as metallic ones (Cu, Ni and their alloys). In order to obtain high exothermic contribution to the heating of powders, the combination “air + polymeric addition (polyethylene) of LDPE grade” was chosen as mixed heat carrier (operating fluid) for the basic version of simulated process. During the analysis of equilibria for the considered multicomponent systems (17 variants), a set of following parameters has been used to characterize the energy intensity of the target powder heating process: the equivalence ratio for reacting mixture and its adiabatic temperature; the energy efficiency of material heating with and without taking into account the effect of fuel addition; specific energy consumption for the powder melting; autothermicity degree of the process during the combined heating (electrothermal heating by the arc of plasma torch and heat flux from the “air + solid fuel additions” mixture) of refractory powders. As a result of the assessment, the preferred (from thermodynamic standpoint) regimes of the considered processes have been found and the possibility to realize an energy-efficient heating of these oxide and metal materials (without oxidation of the latter to CuO, NiO) with a reduced part of the electric channel of energy transfer, resulted from the carrying out of appreciable effect of the fuel-initiated mechanism of heating in the analyzed C–H–O–N–Me-systems, has been shown in the paper.

Keywords: multicomponent C–H–O–N–Me-systems, thermal spraying, spheroidizing, ceramic and metal powder materials, aluminum and chromium oxides, titanium dioxide, copper, nickel, fuel additions, polymers, polyethylene, thermodynamic equilibria, adiabatic temperature, energy efficiency, energy consumptions, autothermicity degree of heating

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Термодинамическая оценка параметров систем C–H–O–N–Me как имитаторов рабочей среды в новых процессах газотермического напыления и сфероидизации порошков

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Реферат. В последнее время ведется разработка группы новых технологий высокотемпературного, в том числе плазменного электродугового, напыления (при атмосферном давлении) и сфероидизации некоторых керамических...
и металлических порошковых материалов как с использованием углеводородных газов в качестве теплоносителей, так и с внесением в высокотемпературную струю органических добавок (в частности, полимерных) для регулирования пористости напыляемых металлических покрытий. В статье рассмотрена возможность модификации процессов данной группы за счет ввода твердотопливных добавок полимерного типа в рабочую среду аппарата для газотермической (плазменной или другой) обработки, обеспечивающей плавление металлических или оксидных порошков. Для этого с помощью термодинамического анализа проведена оценка процессов при температурах (300–3000) К для набора реагирующих пятикомпонентных систем типа C–H–O–N–Me при давлении 0,101 МПа с пятью вариантами Me – алюминий, титан, хром, медь, никель. Это позволяет рассматривать данные системы как имитаторы для потенциальных технологий обработки как оксидных (Al2O3, TiO2, Cr2O3), так и металлических (Cu, Ni и их сплавы) порошков. С целью получения высокого экзотермического вклада в нагрев порошков в качестве смесевого теплоносителя для базового варианта моделируемого процесса выбрано сочетание «воздух + полимерная добавка (полиэтилен марки LDPE)». В ходе анализа равновесий в рассмотренных многокомпонентных системах (17 вариантов) для характеристики энергоемкости целевого процесса нагрева порошков использовали набор параметров: фактор эквивалентности реакционной смеси и ее адиабатическую температуру, энергетический КПД нагрева материала с учетом и без учета вклада топливной добавки, удельные энергозатраты на плавление порошка, степень автотермичности процесса при комбинированном нагреве (электротермическое нагревание через дугу плазмотрона и тепловыделение от смеси «воздух + твердотопливная добавка») тугоплавких порошков. В результате проведенной оценки найдены предпочтительные (с термодинамических позиций) режимы рассмотренных процессов и показана возможность реализации энергоэффективного нагрева данных оксидных и металлических материалов (без окисления последних до CuO, NiO) с пониженной долей электрического канала энергопотеря за счет существенного вклада топливного механизма нагрева в C–H–O–N–Me-системах.

Ключевые слова: многокомпонентные системы C–H–O–N–Me, газотермическое напыление, сфероидизация, керамические и металлические порошковые материалы, оксиды алюминия и хрома, днооксид титана, медь, никель, топливные добавки, полиэтилен, термодинамические равновесия, адиабатическая температура, энергетический КПД, удельные энергозатраты, степень автотермичности нагрева

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**Introduction**

Over the last 5–10 years, specialists in a number of countries (at University of Toronto, Canada, and others) have been intensively developing a group of new high-temperature technologies, including electric arc spraying (at atmospheric pressure, APS) and melting/spheroidizing several ceramic (Al2O3, WC, ZrO2) and metal (copper and its alloys for antibacterial coatings, nickel-based superalloy Inconel 625) powder materials, both using hydrocarbon-based gases (including (CH4 + CO2)-mixtures), and with feeding of solid or liquid organic additions to high-temperature jet [1–8]. Some polymeric materials can be used as these additions in order to control porosity and microstructure of sprayed metal and composite functional coatings (including transpiration cooled ones for heat-resistant blades of gas turbines) [1]. A schematic diagram of a thermal spray system of this type is shown in Fig. 1a.

In this regard, the opportunity to modify the processes of this group is obvious by using the feeding of solid fuel additions (SFA) of polymeric type (which are typically low cost ones) into the operating fluid of these apparatuses for thermal (plasma or other) treatment, purposed for melting of metal or refractory oxide powders under the conditions of gas-powder flow.

![Fig. 1. Variants of schematics of the systems for high temperature processing of metal and ceramic powders, using the polymeric particle additions: a – on the technical description [1] for the process of electric arc plasma spraying of metal/alloy powders; b – analyzed by authors schematic diagram for potential technologies for thermal plasma spraying or spheroidizing of oxide and metal powders with additional feeding of SFA-addition in the processing zone](image-url)
At the same time, it seems acceptable to consider (initially, at a theoretical level) the case of air heat carrier (it acts simultaneously as an oxidizer). It was efficiently used during the recent few years by Russian group [9, 10], based on new arc plasma torches with a power of up to 52 kW for powder spraying of some alloys, oxides and cermet compositions, and, as one of the variants, this technology was used with the combination of air with injection of hydrocarbons (propane-butane or methane) additions into the torch. The chosen variant of the process to consider is schematically illustrated in Fig. 1b.

To execute this task, at the first stage it is expediently to use only thermodynamic analysis of energy consumption parameters of chosen variant of the thermal process. As the simulants of typical thermal treated powders in a high temperature flow, it is suitable to consider a set of three oxide compounds – Al2O3, TiO2, Cr2O3 and two metals – copper and nickel. These substances are widely used in conventional industrial technologies [11] as well as newly developed ones for spheroidizing and plasma spraying of powder materials [1, 2, 4, 8–10, 12].

**Methodology of analysis**

We used the variant of thermodynamic method, which is based on finding the maximum of entropy of reacting system (i.e. minimization of the Gibbs free energy/thermodynamic potential) in the considered equilibrium or quasi-equilibrium systems at specified pressure and temperature regime at the inlet, using such code for chemical thermodynamics analysis as TERRA, developed at Bauman MSTU, Moscow [13, 14]. An algorithm for calculation of thermodynamic states in multicomponent systems with organic and inorganic components is based on the equations:

\[
TdS \geq dU + \delta A \quad \text{or} \quad TdS - dU - pdV \geq 0; \quad (1)
\]

\[
S = \sum_{i=1}^{k+l} S_i^{(p)} n_i + \sum_{j=1}^{k} S_j n_j = \sum_{i=1}^{k+l} \left( S_i^{0} - R_0 \ln \frac{R_0 T_n i}{\nu} \right) n_i + \sum_{j=1}^{k} S_j n_j - U + \sum_{j=1}^{k} U_j n_j = 0; \quad (2)
\]

\[
U_j = \int_{T_0}^{T} C_{v} dT + \Delta_j H_i^{0} (T_0); \quad (4)
\]

where \( T \) – temperature, \( K \); \( S \) – total entropy of the mixture, J·kg\(^{-1}\)·K\(^{-1}\); \( U \) – complete internal energy, J·kg\(^{-1}\); \( A \) – pressure-volume work of the system, J·kg\(^{-1}\); \( p \) – pressure, Pa; \( v \) – specific volume, m\(^3\)·kg\(^{-1}\); \( S_j^{(p)} \) – entropy of gas phase component at the partial pressure which it will have in an equilibrium condition; \( k \) – quantity of components of the gaseous phase; \( L \) – quantity of condensed phases accounted at calculation; \( n_i \) – concentration of the \( i \)th component of the mixture, mol·kg\(^{-1}\); \( S_i \) – entropy of the \( i \)th component of the mixture, J·mol\(^{-1}\)·K\(^{-1}\); \( S_0 \) – standard entropy of gas phase component at temperature \( T \) and \( p = 0.101 \) MPa; \( R_0 \) – the universal gas constant, J·mol\(^{-1}\)·K\(^{-1}\); \( C_{vi} \) – specific heat capacity of the \( i \)th component of mixture at \( v = \text{const} \), J·mol\(^{-1}\)·K\(^{-1}\); \( H_i^{0} \) – standard enthalpy of the \( i \)th component of mixture, J·mol\(^{-1}\); \( b_j \) – mole content of the \( j \)th chemical element at the system, mol·kg\(^{-1}\); \( a_{i} \) – stoichiometric coefficient, i.e. numbers of atoms of chemical element \( j \) in substance \( i \).

During the analysis of thermodynamic equilibria in the multicomponent systems (17 of their variants were considered), a set of the following parameters was used to characterize the energy intensity of desired process of heating and melting of metal-containing powders: the equivalence ratio (ER) of the reacting mixture and its adiabatic temperature \( T_{ai} \); such output parameters as the energy efficiency \( EnE \) of the material heating (in various versions – with and without taking into account the contribution of the fuel addition to the efficiency), specific electrical energy consumption for the heating and melting \( EC \), the degree of autothermcity (in a variant on temperature \( AD_T \) and in a variant on enthalpy \( AD_H \)) for total allothermal process of combined heating of refractory powders (electrothermal heating through an arc of plasma torch and heat transfer from the oxidizing mixture “air + SFA”). Part of these parameters was tested...
earlier for characterization of processes of thermochemical and plasma assisted pyrolysis, gasification and combustion of a number of industrial fuels and wastes, including solid ash-rich fuels [15–21].

The temperature $T_{ad}$ for mixtures with established components of equilibrium system was found based on the following dependences derived from the law of conservation of energy [21]:

$$ I_{pr} (T_{ad}) = I_{in} (T_0); \quad (8) $$

$$ I_{in} (T_0) = \sum_j \left( M_j \Delta_H^0 \right); \quad (9) $$

$$ I_{pr} (T_{ad}) = \sum_i \left( M_i \Delta_H^0 \right) + $$

$$ + \sum_i \left( M_i \int_{T_0}^{T_{ad}} C_{pl}(T) dT \right); \quad (10) $$

where $I_{pr}(T_{ad})$ — sum of the standard enthalpies of formation of obtained products $\Delta H_i^0$ (with taking into account theirs fractions $M_i$ in the product mixture) and the enthalpies of theirs heating from initial temperature $T_0$ to adiabatic $T_{ad}$; $I_{in}(T_0)$ — sum of the standard enthalpies of formation for the initial components $\Delta H_j^0$ (with taking into account theirs molar fractions $M_j$ in the initial mixture); $C_{pl}$ — specific heat capacity for the products.

First variant of the energy efficiency was determined on the basis of the first law of thermodynamics, by analogy with the dependence previously used to describe a similar efficiency (which coincides with CGE (cold gas efficiency)) [16] for plasma gasification of fuels [15–18] with syngas production (based on CO and H$_2$) as the main product

$$ EnE = \frac{LHV_{SG}}{LHV_p + Electricity}; \quad (11) $$

where $LHV_{SG}$, $LHV_p$ — lower heating values for the main product and for the initial fuel; $Electricity$ — total electrical energy consumption in this process during the operation of arc plasma torch and auxiliary electrical equipment. To determine $Electricity$, the calculated difference $(H_{T_2}^0 - H_{T_{ad}}^0)_{pr}$ was used (it was assumed to be equal to the required power of the torch $P_{pl}$) between total enthalpy of the main product at desired operating temperature $T_2$ and the enthalpy of the product at $T_{ad}$.

For the currently considered case of heating of metal or ceramic powders in (11) was modified by introducing into the numerator (instead of $LHV_{SG}$) the quantity of difference of the enthalpies $\Delta H_{Me} = (H_{T_2}^0 - H_{T_{ad}}^0)_{Me}$, which is required to heat the metal or oxide from the temperature of its standard state $T_0$ to the desired specified temperature $T_2$, which exceeds the powder melting temperature $T_1$ by the variable (that characterizes the degree of overheating of the reacting system beyond $T_1$, given below in Part 4), approximately representing the degree of nonadiabaticity of real thermal apparatus in quasicylindrical zone between the plasma torch nozzle and the end of the powder heating area (i. e. the substrate in a case of spraying process). The modified expression was established as the following:

$$ EnE_3 = \frac{G_{Me} \Delta H_{Me}}{G_{FA} LHV_{FA} + P_{pl} \left( \frac{\eta_{el} \eta_{eq}}{\eta_{el}} \right) + } $$

$$ + \left( \frac{N_{eq}}{\eta_{el}} \right) $$

where $G_{Me}$, $G_{FA}$ — mass flow rates of the metal (ceramic) powder and fuel addition; $LHV_{FA}$ — lower heating value of the fuel addition; $P_{pl}$ — electric power on an arc of plasma torch; $N_{eq}$ — power of the auxiliary electrical equipment (in this case, air compressor); $\eta_{el}$ — thermal efficiency of the torch (assumed equal to 0.80 based on aggregated data for non-transferred arc plasma torches, including ones for thermal spraying [22]); $\eta_{eq}$ — energy efficiency of commercial-scale solid fuel power plants CPP (it was chosen as 0.393 according to the actual reference data from DOE/NETL of USA) [23]. The thermodynamic properties of the reagents (in particular, $\Delta H_{Me}$) were determined using the NIST’s thermodynamic database [24].

The calculated values for the case of the energy efficiency $EnE_3$ (assuming a zero contribution of the “fuel term” to the efficiency value) represent one of the feasible scenarios in which the cost of the consumed fuel addition will be close to negligible level, that will ensure an increase of the $EnE_3$ efficiency magnitude in the considered regime of combined heating.
Moreover, the equivalence ratio for the mixture was used (that contains a fuel addition, which is decomposed in a redox reaction during the heating) as a useful initial parameter to characterize oxygen-containing reacting mixtures [19]

$$ER = \frac{G_{ox}}{G_f} \frac{R_{st}}{R_{si}}$$

where $G_{ox}/G_f$ – ratio of the mass flow rates of oxidizer and fuel for the analyzed reacting mixture; $R_{st}$ – ratio of the flow rates of these reagents in the stoichiometric mixture, which is sufficient for complete fuel oxidation.

The calculation of energy consumption during the operation of a low-pressure compressor for air blowing into the thermal treatment system (in this case, to the plasma torch) was carried out according to the conventional method [25], at the value of polytropic index of 1.40. Also, for the “basic” (further labeled as “bas”) modes (in the N$_2$ environment, that simulates the regimes of industrial plasma spraying units [11] without fuel additions) of high-temperature processing of powders, we took into account the energy consumption in the technological chain for producing nitrogen from air, and by analogy with [20] it was assumed at the level of 0.3 kW-h/kg (ignoring the contribution of the CPP energy efficiency).

Choice of polymeric solid fuel addition for the analyzed process

The combination of air + (polymer addition – polyethylene (commercial LDPE grade, i. e. low density PE)) was chosen as a mixed heat carrier for the main variant of the simulated thermal process to ensure high exothermic effect to the powder heating. At the same time, it is important that reclaimed powdery (dusty) polyethylene of technical purity, according to the environmental classifiers of some regions (e. g. CIS countries), belongs to non-hazardous industrial wastes [26] and is typically supplied from petrochemical (organic synthesis) plants to large-scale consumers at prices close to zero. Tab. 1 demonstrates the characteristics of this variant of polymer addition in a comparison with the properties of some related substances to illustrate the preference of LDPE as a potentially better solid fuel.

### Table 1

| Material or compound (commercial grade) | Formula; mass fraction of non-carbon part | $HHV$, MJ/kg | $LHV$, MJ/kg | $\Delta f^oH$, MJ/kg |
|----------------------------------------|------------------------------------------|--------------|--------------|------------------|
| Polystyrene (PS, PS-waste)             | (C$_8$H$_8$)$_n$; 0.077                  | 40.00–43.65 [27–28] | 38.30–41.96 [27–29] (†) | –1.18 (at $HHV = 40.0$ [27]), and the close value on [30] |
| Low density polyethylene (LDPE, LDPE-waste) | (C$_2$H$_4$)$_n$; 0.144 | 46.00–47.74 [27–29] | 42.8–44.6 [27–29] (†) | –2.073 [31] |
| Polyamide oxygen-containing polymer (polycaprolactam grade, PA6) | (C$_6$H$_{11}$NO)$_n$; 0.363 | 30.0–30.9 [28, 32] | 28.8 [28, 32] | –2.911 (on the data [24])† |
| Cellulose                              | (C$_6$H$_{10}$O$_5$)$_n$; 0.556         | 17.5 [33–34] | 16.0 [35–36] (†) | –5.95 [37] |
| Graphite                               | C; 0                                    | 32.8 [24] | 32.8 [24] | 0 |
| Methane                                | CH$_4$; 0.251                          | 55.5 [24] | 50.0 [24] | –4.67 [24] |

† Data for monomer.

**Symbol:** † – calculated on the equation: $LHV = HHV − 0.21978H$ [38] (H – hydrogen fraction in the compound, wt. %).

### Results of thermodynamic modeling

The obtained results for the energy consumption parameters of the heating (with melting of processed oxide and metal powders) for different variants of the C–H–O–N–Me systems (Me = Al, Ti, Cr, Cu, Ni; and the minor fraction of Ar was also taken into account (as air component) for all systems) are presented in the Tab. 2, and the examples of calculated data on equilibrium chemical composition of products during heating of the systems of this class (in a temperature range up to 3000 K) are shown in Fig. 2–4 (condensed phases are indicated by the symbol “c”).
Established energy consumption parameters for heating of different variants of the C–H–O–N–Me-systems (Me = Al, Ti, Cr, Cu, Ni) at pressure $p = 0.101$ MPa

| Number of calculated reacting mixture and heated ceramic/metal powder | 1 – Cr$_2$O$_3$ | 2 – Cr$_2$O$_3$ | 3 (bas) – Al$_2$O$_3$ | 4 – Al$_2$O$_3$ | 5 (bas) – Al$_2$O$_3$ | 6 – TiO$_2$ | 7 (bas) – TiO$_2$ | 8 – Cu | 9 (bas) – Cu | 10 – Ni | 11 – Ni | 12 – Ni | 13 (bas) – Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Operating gas / use of fuel addition in the mixture | Air / + | Air / + | N$_2$ / – | Air / + | N$_2$ / – | Air / + | N$_2$ / – | Air / + | N$_2$ / – | Air / + | N$_2$ / – | Air / + | N$_2$ / – |
| Mass fraction of (MeO/Me)-powder in the mixture | 0.584 | 0.483 | 0.667 | 0.483 | 0.667 | 0.483 | 0.667 | 0.631 | 0.800 | 0.358 | 0.317 | 0.323 | 0.800 |
| Melting point of (MeO/Me)-powder $T_m$, K | 2708 | 2708 | 2708 | 2328 | 2328 | 2130 | 2130 | 1359 | 1359 | 1729 | 1729 | 1729 | 1729 |
| Desired specified temperature of the powder $T_d$, K | 2850 | 2850 | 2850 | 2500 | 2500 | 2300 | 2300 | 1500 | 1500 | 1900 | 1900 | 1900 | 1900 |
| Difference of enthalpies $H_{f298}^\circ$ – $H_{f0}^\circ$, MJ/kg of powder | 2.326 | 2.326 | 2.326 | 3.374 | 3.374 | 2.120 | 2.120 | 0.560 | 0.560 | 0.915 | 0.915 | 0.915 | 0.915 |
| Equivalence ratio for redox reaction with fuel $ER$ | 0.961 | 0.961 | 0 | 0.961 | 0 | 0.961 | 0 | 0.971 | 0.894 | 0.271 | 0 |

| Adiabatic temperature $T_{ad}$ for reacting mixture, K | 1458 | 1651 | 300 | 1467 | 298 | 1616 | 348 | 1495 | 298 | 1895 | 1895 | 1895 | 994 | 298 |
| Condensed products in the reacting mixture at $T_2$ | Cr$_2$O$_3$(c) | Cr$_2$O$_3$(c) | Cr$_2$O$_3$(c) | Al$_2$O$_3$(c) | Al$_2$O$_3$(c) | TiO$_2$(c) | TiO$_2$(c) | Cu(c) | Cu(c) | Ni(c) | Ni(c) | Ni(c) | C(c) | Ni(c) |
| Degree of overheating (DOH) of the reacting system beyond $T_2$, J/J | 1.214 | 1.244 | 1.187 | 1.113 | 1.084 | 1.072 | 1.060 | 1.123 | 1.120 | 1.104 | 1.098 | 1.077 | 1.111 |
| Energy efficiency for heating process $EnE_1$, J/J | 0.114 | 0.091 | 0.121 | 0.187 | 0.188 | 0.143 | 0.125 | 0.281 | 0.112 | 0.147 | 0.115 | 0.024 | 0.124 |
| Energy efficiency $EnE_2$ (ignoring the contribution of CPP energy efficiency), J/J | 0.244 | 0.189 | 0.278 | 0.362 | 0.427 | 0.263 | 0.282 | 0.283 | 0.234 | 0.148 | 0.116 | 0.034 | 0.276 |
| Energy efficiency $EnE_3$ (ignoring the contribution of SFA enthalpy), J/J | 0.127 | 0.103 | 0.121 | 0.225 | 0.188 | 0.180 | 0.125 | 1.401 | 0.112 | 0.760 | 0.636 | 0.045 | 0.124 |
| Electric energy consumption $EC_1$, kW-h/kg of powder | 5.094 | 6.277 | 5.332 | 4.170 | 4.995 | 3.268 | 4.728 | 0.111 | 1.394 | 0.335 | 0.400 | 5.645 | 2.052 |
| Electric energy consumption on $EC_2$ (ignoring the contribution of CPP energy efficiency), kW-h/kg of powder | 2.002 | 2.467 | 2.096 | 1.639 | 1.963 | 1.284 | 1.858 | 0.044 | 0.548 | 0.132 | 0.157 | 2.218 | 0.807 |
| Degree of autothermicity of the reacting system on temperature $AD_{D_2}$, K/K | 0.454 | 0.530 | 0 | 0.531 | 0 | 0.659 | 0 | 0.996 | 0 | 0.997 | 0.997 | 0.435 | 0 |
| Degree of autothermicity on enthalpy $AD_{d_2}$, J/J | 0.272 | 0.313 | 0 | 0.418 | 0 | 0.531 | 0 | 0.999 | 0 | 0.997 | 0.997 | 0.556 | 0 |

Footnote. $DOH = (I_{ad}(T_2) – I_{ad}(T_0)) / (I_{ad}(T_3) – I_{ad}(T_0)); \ EC_1 = (((P_{el} / \eta_{el})) + (N_{eq} / \eta_{el})) / G_{d2}; \ EC_2 = (P_{el} / \eta_{el}) + N_{eq} / G_{d2}$.  

According to the results of the analysis of seventeen system variants, it was found that for the regimes simulating the melting of metals in air-fuel mixtures (containing mainly CO$_2$, H$_2$O and N$_2$ gases with small admixture of CO and H$_2$), the parameters of energy efficiency of the process, such as $EnE_1$ and $EnE_2$, are obviously higher, than for standard (endothermic) modes of their processing in N$_2$ (as, for example, on industrial plasma spraying modules of the UPU-3D type [11]).
Fig. 2. Calculated dependences for the chemical composition of equilibrium C–H–O–N–Al (a) and C–H–O–N–Ti (b) systems at the range of 300–2500 K (at pressure $p = 0.101$ MPa) at the ratio of flow rates of initial components, corresponding to the process regimes No 4 and No 6 in the Tab. 2.

Fig. 3. Calculated dependences for the chemical composition of equilibrium C–H–O–N–Cu (a) and C–H–O–N–Ni (b) systems at the range of 300–2000 K (at pressure $p = 0.101$ MPa) at the ratio of flow rates of initial components, corresponding to the process regimes No 8 and No 10 in the Tab. 2.

Fig. 4. Calculated dependence for the chemical composition of equilibrium C–H–O–N–Cr-system at the range of 300–3000 K (at pressure $p = 0.101$ MPa) at the ratio of flow rates of initial components, corresponding to the process regime No 1 in the Tab. 2.

The specific energy consumption for the cases of heated metals is correspondingly lower than for these “basic regimes” in N$_2$-heat carrier gas (at the mass fraction of Me-powder in reacting mixture of 0.800).

For the case of the considered oxide processing regimes, their output parameters ($EnE_1$, $EnE_3$), energy consumptions $EC_1$ and $EC_2$) do not differ so much from the “basic regimes” in N$_2$-gas media, but still exceed them in efficiency, at least at the mass fraction of powder in the reacting mixture above 0.58 for heating regimes of Cr$_2$O$_3$ and above 0.48 for the regimes with Al$_2$O$_3$ and TiO$_2$ powders. Here, the achieved degree of autothermicity of the system (in a variant on enthalpy) during the heating $ADH$ does not fall outside the range of 0.27–0.53 for these cases.

**CONCLUSIONS**

1. As a result of theoretical assessment, fulfilled for a set of C–H–O–N–Me-systems, we found preferable regimes, from the point of view of chemical thermodynamics method, for the group of thermal treatment processes (for the example of high-melting oxides of aluminum, chromium and titanium, and copper and nickel metals), which are interesting for technologies of powder spraying and spheroidizing. The processes include melting of the ceramic and metallic materials in gaseous
media formed by the products of air oxidation of solid fuel polymeric addition.

2. The tentative opportunity to arrange an energy-efficient heating of the considered materials (moreover, without oxidation of the condensed phase of considered metals to their oxides CuO, Cu₂O, NiO) was detected at the minimized electric channel of energy transfer (in a comparison with industrially standard (“basic”) regimes of powder melting in nitrogen plasma jet), due to the using the efficient fuel-derived heating channel in these C–H–O–N–Me-systems, which contain the fuel addition.

3. It is shown, based on the results of the analysis of the selected systems, that for the modeling regimes of the melting of Cu and Ni powders in the air-fuel mixtures, the process efficiency parameters, including energy efficiency and energy consumption per unit of the metal are significantly better than for standard (“basic”) regimes of their high-temperature processing (in N₂ medium). For the case of oxide processing regimes, in terms of the calculated output characteristics of the process (\(EnE_1\), \(EnE_3\), energy consumption), they differ less substantially from the standard heating regimes (in N₂), but also surpass them in the efficiency (the value of energy consumption \(EC_2\) does not exceed 2.0 kWh per kg of oxide), despite the moderate level of the found degree of autothermicity \(ADH\) for the process – 0.27–0.53 (in a contrast to the \(ADH\), which is close to one for the Cu and Ni melting regimes in the highly oxidized gas mixtures at the level of equivalence ratio of the mixtures \(ER \geq 0.97\), in which the fuel is almost completely decomposed to CO₂ and H₂O products).

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