CHARACTERIZATION OF OPPORTUNITY FOR UPGRADING OF THE SYSTEM BASED ON ARC PLASMA TORCH FOR THERMAL SPAYING OF CERAMIC MATERIALS, BY MEANS OF USE OF FUEL VORTEX INTENSIFIER.

PART I: THERMODYNAMIC MODELING OF THE SYSTEM EFFICIENCY PARAMETERS

Abstract. One of the main trends in the field of improving the modern technologies of thermal spraying, including plasma one, for functional ceramic coatings formation is the reducing the energy consumption of the process. In this regard, one of the important directions for improving these technologies is the development of their new versions, using the principle of adding inexpensive fuel-oxidizer mixtures based on hydrocarbons with air. This type of plasma-fuel type of spraying will be promising for application at the present time, first of all, in order to obtain refractory functional coatings. For this purpose, we investigated the opportunity for upgrading an industrial unit/system for plasma spraying of ceramic powder materials with arc plasma torch of 25–40 kW power by the use of experimental variant of a fuel gas-vortex intensifier. The thermodynamic assessment of possible parameters of the generated mixed flow after the torch with this fuel intensifier was carried out to estimate the applicability of this system to optimize the spraying of oxide and carbide coatings (based on the examples of Al₂O₃, Cr₃C₂ and other powders). The analysis of possible parameters of the produced flow after the torch with intensifier was performed for the cases of main C–H–O–N–Ar–Me (Me = Al, Cr) systems and additional C–H–O–Al-system to assess the potential of this system to modify the technology of oxide and carbide ceramic coatings formation. New regimes, which were analyzed in our research as the simulants of Al₂O₃ spraying, surpass on calculated energy efficiency characteristics (by 10–20 %) one of the new prospective spraying methods with (CO₂+CH₄)-plasma, as well as the conventional method of powder heating during the spraying with N₂-plasma. The case of our proposed fuel assisted process (FA-APS) with liquefied petroleum gas (LPG) fuel for the heating of ceramic powders (especially, Al₂O₃) demonstrates the advantage of the process (in particular, on the energy efficiencies and energy consumption) in a comparison with the conventional regimes of APS of the powders (in N₂ plasma of the standard torch). For the variants of the FA-APS with Al₂O₃ and Cr₃C₂ feedstock powders it was established to be potentially possible to obtain (at the moderate values of total electric energy consumption for the torch and auxiliary equipment, – near 1.8 and 1.0 kWh/(kg of product)) such high level of the process productivity on the final product as approximately 17 and 28 kg/h, respectively; at the values of required power of the torch: ≥ 28.2 and ≥ 22.3 kW.

Keywords: electric arc torch, combustion assisted plasma spraying, oxide and carbide powders, thermodynamics, energy efficiency, energy consumption

process. Such a plasma-top fueling system has the highest potential for the formation of functional coatings, such as ceramic, metallic, and composite materials, as well as for the development of new technologies for the sprayed plasma. This is a promising area of research, and the development of new plasma spraying technologies is one of the most important trends in coating technologies. A number of new technologies have been actively developed in this field (Oerlikon Metco AG and Praxair Surface Technologies), including plasma spraying, according to the data of leading companies in the world market for thermal spraying processes, the predominant starting equipment and technologies for thermal spraying reached the end of the 2010s a level of $10 billion/year, while in 2010 this value was no more than 4–5 billion [1–3]. At present, the main part (near 45%) of thermal spraying processes is plasma ones based on the use of DC arc torches. The prevalent starting materials for thermal spraying, including plasma spray, according to the data of leading companies in this field (Oerlikon Metco AG and Praxair Surface Technologies), are powders, of which about 10^5 tons are used annually. A significant part of them are ceramic powders, including Al₂O₃ ones. The disadvantages that restrain their industrial adoption (and other oxide coatings) are, along with moderate adhesion to the metal substrate and the complexity of control of the properties of coating formed, also the high energy consumption for the process (15–35 kW/h per kg of sprayed material) and typically insufficient coefficient of powder utilization under the spraying due to its instable heating and limited residence time of particulates in a high temperature zone [1, 3, 4]. In this regard, one of the important directions for improvement of spraying technologies is to optimize the conditions for heat and mass transfer of powders with plasma, in particular, by optimization of operating modes of electric arc plasma torches (EAPTs) for spraying in terms of temperature and velocity characteristics and the composition of used plasma gases or their mixtures.

In the last 10 years, in a number of countries (in Canada, USA, Russia, Spain, Japan) within the scope of this important trend in coating technologies, a group of new technologies have been actively developing [4–9] for electric arc spraying (at atmospheric pressure, APS) and of spheroidizing of ceramic (Al₂O₃, ZrO₂, TiO₂, rare earth oxides, WC) and metal (copper alloys for antibacterial coatings, heat-resistant nickel alloys) powder materials, as well as the use of hydrocarbon based heat-transport gases (including CH₄ + CO₂ mixtures) to improve velocity and thermal conductivity of plasma jets and to intensify particle melting in them, as well as with organic solid or liquid additives injection into plasma to control porosity and structure of sprayed coatings [10–14].

In connection with the aforementioned trends in thermal (including plasma) spraying, it seems promising to develop new processes of this type using the principle of injection (into the heat-transport medium in devices for spraying metal or oxide powders) of inexpensive fuel-oxidizer mixtures, based on alkanes (natural gas (NG), etc.) with air, that are efficient in terms of thermophysical
properties, from analogy with [7, 8]. In our opinion, it is expedient to use such plasma-fuel variety of spraying, first of all, to obtain such functional coatings as wear-resistant coatings of machine-building parts based on Al$_2$O$_3$, as well as carbides (of chromium, etc.), as the most demanded in recent years due to combination of technical and economic parameters for a number of factories, in particular, for the manufacturing of power plant and oil-producing equipment, including in Belarus and CIS [1, 3, 7].

Previously, we performed the analysis using thermodynamic method for processes in C–H–O–N–Me systems in the range of 300–3000 K. This problem statement allows considering them as simulators of operating gas-particulate media for technologies of oxide and metal powder processing, including spraying and powder spheroidizing [15]. This approach can be also efficient for the task stated in this research: to determine (based on theoretical assessment and subsequent experiment) the possibility for upgrading of typical for CIS systems/installations for spraying of ceramic powder materials (oxides, carbides) based on EAPT of 25–40 kW power [1, 3] by means of use of trial variant of fuel gas-vortex intensifier to a level that gives a prospect for application of these systems in machine industry.

**Plasma torch based spraying system, intended for the upgrading by means of use of the vortex-fuel intensifier.** The experimental system was developed based on standard industrial plasma spraying unit of UPU-3D type [1, 3] with special fuel intensifier for testing with the injection of combination of compressed gases – nitrogen and mixture of liquefied petroleum gas (LPG) with air. A schematic diagram of a spray system of this type is illustrated in Figure 1. In this case, the operating regimes can be used with variation of power of the DC plasma torch ($P = 25–35$ kW with electric current on the arc up to $350–400$ A) as well as with variation of the composition of outlet high-temperature jets, due to the injection of ($N_2 + (\text{air} + \text{LPG})$) gas mixture into the apparatus used. The mixture can be injected through the special vortex-type fuel intensifier (the body of which made from Cu–Zn alloy L63), that was designed taking into account the experience of a number of DC torches of 50–200 kW power [16–19] for plasma chemical reactors for pyrolysis and oxidation of hydrocarbons. In particular, the basic operating regime of the upgraded system based on the UPU-3D unit allows, as the most preferable, such flow rate of nitrogen for plasma stabilization in the torch as $G_{N_2,pl} = (1.0–1.2) \cdot 10^{-3}$ kg/s, and the flow rate of this gas for sprayed powder transportation from the feeder as 10–15% of the $G_{N_2,pl}$ value. These parameters of the proposed spraying system were further used as the initial conditions for our thermodynamic calculations.

**Modeling method for assessment of the parameters of high-enthalpy flow in the spraying unit based on EAPT with the fuel intensifier to determine the applicability of this system (as applied to oxide (Al$_2$O$_3$) and carbide (Cr$_3$C$_2$) materials).** The thermochemical process with the participation of gas fuel in the reaction mixture for the basic case of C–H–O–N–Me systems under consideration (Me = Al, Cr; in this case, the presence of an Ar impurity as air component is also advisable to take into account [20]) under the conditions of the spraying process at ambient pressure ($p = 0.101$ MPa) is quite complicated in terms of kinetics and it can be presented by a simplified brutto-reaction (assuming that the ceramic (solid) part of the mixture, for example, oxide one, is not subjected to chemical transformations up to its melting point):

$$
\alpha N_2(\text{gas}) + \beta C_{x_1}H_{y_1}(\text{gas}) + \gamma N_{x_2}O_{y_2}Ar_{z_2}(\text{gas}) + \delta Al_2O_3(\text{solid}) = \\
= \varepsilon C_{x_2}H_{y_2}O_{z_2}N_{w_2}Ar_{z_3}(\text{gas}) + \delta Al_2O_3(\text{liquid}).
$$

(1)

Here $C_{x_1}H_{y_1}$ and $N_{x_2}O_{y_2}Ar_{z_2}$ are elemental formulae of technical grade LPG and air; and it was accepted that impurities of steam and CO$_2$ in air after a compressor with standard oil-moisture separator can be neglected. Taking into account the complexity of set of redox reactions in gas phase of the system due to the possibility of several dozen compounds participation in them at different temperatures, in a general
case the set can be represented by quite simplified brutto-reaction, which, by analogy with [19], allows partial as well as complete oxidation of alkane fuel molecules:

\[ C_4H_{11} + n_1H_2O + n_2(O_2 + 3.76N_2) = p_1H_2 + p_2CO + p_3H_2O + p_4CO_2 + p_5CH_4 + p_6N_2 + p_7NO + p_8C(\text{solid}). \]  

(2)

The composition of selected fuel (LPG) was taken for further calculation based on the experimental data [16] for this feedstock: CH₄ = 0.6; C₂H₆ = 5.6; C₃H₈ = 72.5; n-butane C₄H₁₀ = 12.2; iso-butane – 9.0 (in vol.%). Its averaged molecular weight is 0.0461 kg/mol, lower heating value (LHV) = 46.2 MJ/kg. Taking this into account, for the reaction (1), as well as those similar to it, the values of the coefficients in elemental formulas of the reagents were established as follows: \( x_1 = 3.144, y_1 = 8.288, x_2 = 1.561, \) \( y_2 = 0.420, z_2 = 0.0094. \) Wherein, in the general case, the coefficients for elemental formula of complete heterogeneous mixture of reaction products CₓHᵧOᵦNᵦArᵦMeᵦk can be expressed as follows: \( x = \beta \cdot x_1, \) \( y = \beta \cdot y_1, \) \( z = (\gamma \cdot y_2 + 3\delta), \) \( w = (2\alpha + \gamma \cdot x_2), \) \( v = \gamma \cdot x_2, \) \( k = 2\delta \) (for systems with Al₂O₃); and \( x = (\beta \cdot x_1 + 2\delta), \) \( y = \beta \cdot y_1, \) \( z = \gamma \cdot y_2, \) \( w = (2\alpha + \gamma \cdot x_2), \) \( v = \gamma \cdot x_2, \) \( k = 3\delta \) (for systems with Cr₃C₂).

During the thermodynamic analysis, which makes it possible to predict probable products under equilibrium and quasi-equilibrium conditions with acceptable accuracy over a wide range of temperature (up to 6000 K), without considering the mechanisms of possible reactions, we used the variant of this method based on finding of entropy maximum (i.e. minimization of the Gibbs free energy/thermodynamic potential) of reacting system. The calculations were carried out using TERRA code [19, 20]. The algorithm used in it for determining the atomic/molecular composition and properties of reacting systems was presented in [15]. The data calculated were further used to analyze the efficiency of the target process of heating ceramic powders in these systems, and herewith a special group of energy and processing parameters was used, including the following ones: equivalence ratio of the mixture (on fuel) \( ER \) [15, 21] and its adiabatic temperature; the energy efficiency of the material heating (in various versions – with and without taking into account the contribution of fuel to the efficiency value), specific energy consumption \( EC \) for the heating to desired (specified) temperature of the process, the degree of autothermicity of total allothermal process (in a variant on temperature \( AD_T \) and in a variant on enthalpy \( AD_H \)) during the combined powder heating. The informativeness of these parameters was earlier tested during generalization of the characteristics of thermochemical and plasma processes, such as pyrolysis (typically requiring intensive allothermal heating via electrothermal or other routes) and gasification and combustion of a number of fuels and carbonaceous wastes, including high-asph ones [15, 21–24].

For a typical variant of heating (during spraying) of ceramic powders, in particular, oxides, the expression for such parameter as the energy efficiency \( En_{E_1} \) is derived taking into account the first law of thermodynamics, and in it (in contrast to the similar efficiency for gasification of solid fuels [19, 22–24]) it is advisable to use in the numerator the enthalpy difference \( \Delta H_{\text{MeO}_x} = \left(H_{T_2} - H_{298}\right)_{\text{MeO}_x} \), required to heat the oxide from temperature \( T_0 \) to the desired (specified) temperature of the process \( T_3 \), which exceeds the melting point of oxide \( T_2 \) by an amount (characterizing the degree of overheating of the reacting system beyond \( T_2 \) (DOH)), which schematically represents the degree of nonadiabaticity of spraying apparatus in a zone between plasma torch nozzle (i.e. anode outlet) and the end of powder heating area (i.e. substrate for spraying). The final expression for this efficiency is the following:

\[
En_{E_1} = \frac{G_{\text{MeO}_x} \Delta H_{\text{MeO}_x}}{(G_f LHV_f) + \left[ \frac{P_{pt}}{(\eta_{el} \eta_{pt})} \right] + \left[ \sum_k N_{(\text{aqo}))_k} \right] / \eta_{el}).
\]

(3)

Here \( G_{\text{MeO}_x} \) and \( G_f \) are mass flow rates for ceramic powder and for fuel, \( LHV_f \) is lower heating value of the fuel, \( P_{pt} \) is electric power on an arc of the torch, \( N_{\text{aqo}} \) is power (or energy consumption) for each type of auxiliary electrical equipment in the system (in our case, these are: a) the power of air compressor and b) the consumption of electricity for cryogenic production of \( N_2 \) as a plasma gas for the torch), \( \eta_{el} \) is thermal efficiency of the torch (assumed equal to 0.80 based on aggregated data for non-transferred arc plasma torches [25]), \( \eta_{el} \) – energy efficiency of commercial-scale solid fuel power plants CPP of steam turbine cycle (it was chosen as 0.393 according to the actual reference data from DOE/NETL) [26]. The thermodynamic properties of the reagents (\( \Delta H_{\text{MeO}_x} \), etc.) were determined using the NIST’s database [27].
As additional indicators of the energy efficiency of the upgraded spraying system, we used, by analogy with [15], the energy efficiency \(\text{EnE}_2\) (which differs from \(\text{EnE}_1\) by ignoring the real energy efficiency of CPP (i.e. by using such efficiency magnitude as \(\eta_{el} = 1\) on the efficiency value \(\text{EnE}_2\)), and the energy efficiency of \(\text{EnE}_3\) (calculated, in a contrast with \(\text{EnE}_1\), without taking into account the effect of fuel enthalpy on the last efficiency, i.e. with \(G_1 \cdot LHV_1 = 0\)). The power consumption of the compressor for air blowing into the spraying system was calculated as in the paper [28], at the polytropic index of 1.40. Also, for the “basic” (further labeled as “bas”) regimes (in \(N_2\), that simulates the conditions of industrial spraying units [1, 3] without fuel in plasma flow) of powder processing, we took account of the energy consumption for production of \(N_2\) from air, and by analogy with [29] it was assumed to be at the level of 0.3 \(\text{kW} \cdot \text{h/kg}\) (ignoring the contribution of the CPP efficiency).

The adiabatic temperature \(T_{ad}\) of a mixture of given composition under equilibrium and quasi-equilibrium conditions can be calculated in the mass-average approximation based on the dependences derived from the law of conservation of energy [15, 24]. Specific consumption of electric energy (in kWh (for all types of equipment in the system) per kg of final ceramic material) in systems of the type under consider-

\[
N_0 = Q_{\text{hm}} + Q_w + Q_{\text{ex}} = \left( \Delta H_1^m + \Delta H_2^m + \Delta H_3^m + \Delta H_4^m + \Delta H_5^m \right) + Q_w + Q_{\text{ex}}.
\]

Here in the considered general case of this air-plasma APS-process (in which, as an option, heating of the zone under consideration: (excluding the contribution of the CPP efficiency) was calculated as \(EC = (P_{\text{pl}}/\eta_{el} + \sum N_{\text{mex}})/G_{\text{MeOx}}\), and the degree of overheating (\(J\)) of the reacting system beyond \(T_2\) (i.e., to the desired specified temperature of the process \(T_3\) as: \(\text{DOH} = (I_{\text{pr}}(T_2) - I_{\text{pr}}(T_0))(I_{\text{pr}}(T_1) - I_{\text{pr}}(T_0))\). Here, \(I_{\text{pr}}(T)\) denotes three variants of the sum of enthalpies of equilibrium products of interaction (taking into account their molar fractions \(M_f\) in the reacting mixture): at high temperatures \(T_2\) and \(T_3\), and at initial \(T_0 = 298.15\ \text{K}\).

For most general case of the considered APS process (assuming the use of thermally dissociated feedstock/material in it), the energy balance for the main (thermochemical) zone under the spraying of ceramic (e.g. oxide) material, during which the target transformation takes place (including possible chemical dissociation reaction and the phase transition, i.e. melting of oxide) can be written as:

\[
N_0 = Q_{\text{hc}} + N_{\text{hm}} = Q_{\text{hc}} + \sum(M_f \ H_f) \quad \text{(where } Q_{\text{hc}} \text{ is the thermal power of the material (if it is injected as preheated one), } N_{\text{hm}} \text{ is the thermal power of the heat transport gas, i.e. plasma gas, preheated by the torch arc); } Q_{\text{hm}} \text{ – “useful” heat, transferred from hot gas in the considered jet to the initial particulates heated to melting (which depends on the material can be exposed to disso-

\[
\Delta H_1^m = (H_1^0 - H_0^0)_{\text{hm}}, \quad \text{is the difference between the enthalpy of the initial material (undissociated) at } T_1 \quad \text{(e.g., for the case of Al(OH)\_3 equal to } \sim 550\ \text{K [32]) and its enthalpy at } T_0; \quad \Delta H_2^m = \Delta H_2^{0\298} \text{ is the heat of dissociation reaction (endothermic) of the initial feedstock powder (e.g. with the formation of oxide) at } T_1; \quad \Delta H_3^m = (H_3^0 - H_1^0)_{\text{hm}}, \quad \text{is the difference between the enthalpy of dissociated powder at the } T_2 \text{ and its enthalpy at } T_1; \quad \Delta H_4^m = (\Delta t H_{\text{liquid}}^0 - \Delta t H_{\text{solid}}^0) = \Delta H_{\text{melt}}^0 \text{ – is the heat (normalized to the standard conditions) of powder melting at } T_2; \quad \Delta H_5^m = (H_5^0 - H_1^0)_{\text{hm}}, \quad \text{is the difference between the enthalpy of final powder at } T_3, \text{ slightly higher (usually, for technological reasons, by } 150–300\ \text{K) the } T_2, \text{ and its enthalpy at } T_2.
\]
### Efficiency parameters for C–H–O–N–Ar–Me-systems (Me = Al, Cr) and C–H–O–Al-system as the simulants for the regimes of thermal plasma spray process for oxide and carbide coatings with use of the fuel intensifier

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Regime number of modeling mixture and type of initial ceramic powder material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of operating gas / flow rate of gas for arc stabilization in the torch (g/s) / use of fuel in the initial mixture</td>
<td>Air+ N₂ / the same that #1 N₂ / 1.20 (N₂)/ LPG / the same that #1</td>
</tr>
<tr>
<td>Fraction of initial powder in the mixture γ_{fm}, kg/kg</td>
<td>0.500 0.620 0.620 0.650 0.650 0.800 0.800 0.800 0.620</td>
</tr>
<tr>
<td>Fraction of final product in the product mixture at T₃ γ_{fm}, kg/kg</td>
<td>0.500 0.620 0.620 0.425 0.425 0.800 0.800 0.800 0.620</td>
</tr>
<tr>
<td>Fraction of fuel in the mixture γ_{hf}</td>
<td>0.017 0.013 0.011 0.013 0.011 0.011 0.047 0.064</td>
</tr>
<tr>
<td>Melting point of the product T_{mp}, K</td>
<td>2328 2328 2328 2108 2108 2108 2108 2108 2328</td>
</tr>
<tr>
<td>Desired specified temperature T₃, K</td>
<td>3.37 3.37 3.37 5.82* 5.82* 1.71 1.71 1.71 3.37</td>
</tr>
<tr>
<td>Oxidizer – fuel equivalence ratio ER [21]</td>
<td>1.050 1.050 0 0.300 0.500 0 0 0 0</td>
</tr>
</tbody>
</table>

### Initial parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Regime number of modeling mixture and type of initial ceramic powder material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensed products in the reacting system at T₂ and T₃ temperatures</td>
<td>Al₂O₃ Al₂O₃ Al₂O₃ Al₂O₃ Al₂O₃ Cr₃C₂ Cr₃C₂, Cr₃C₂, C(s) † Al₂O₃ Al₂O₃</td>
</tr>
<tr>
<td>Adiabatic temperature of the system T_{ad}, K</td>
<td>986 837 298 365 300 699 827 275 370 375</td>
</tr>
<tr>
<td>Degree of overheating (DOH) of the system beyond T₂, J/J</td>
<td>1.100 1.095 1.080 1.098 1.106 1.110 1.106 1.117 1.117 1.117</td>
</tr>
<tr>
<td>Energy efficiency of process EnE₁, J/J</td>
<td>0.167 0.197 0.175 0.158 0.154 0.172 0.179 0.183 0.114 0.102</td>
</tr>
<tr>
<td>Energy efficiency of process EnE₂, J/J</td>
<td>0.381 0.461 0.446 0.385 0.391 0.390 0.413 0.467 0.242 0.209</td>
</tr>
<tr>
<td>Energy efficiency of process EnE₃, J/J</td>
<td>0.181 0.208 0.175 0.164 0.154 0.186 0.192 0.183 0.130 0.121</td>
</tr>
<tr>
<td>Energy consumption EC, kW·h/kg of product</td>
<td>2.037 1.772 2.101 3.888 4.136 1.000 0.969 1.015 2.831 3.045</td>
</tr>
<tr>
<td>Degree of autothermicity AD₅₇, J/K</td>
<td>0.312 0.245 0 0.030 0 0.200 0.264 0 0.033 0.035</td>
</tr>
<tr>
<td>Degree of autothermicity AD₅₇, J/J</td>
<td>0.249 0.180 0 0.083 0 0.130 0.174 0 0.079 0.098</td>
</tr>
<tr>
<td>Ratio (H/C) for the initial mixture</td>
<td>–109.5 –125.9 0 –131.13 0 –3.68 –3.78 0 –5.257 –4.409</td>
</tr>
<tr>
<td>Required minimal power of plasma torch (at its efficiency η_pl = 0.8) Pₚₜ₁, kW</td>
<td>19.78 28.23 13.49 25.64 20.37 22.31♦ 29.64♦ 16.24 11.15♦ 9.83♦</td>
</tr>
<tr>
<td>Required minimal power of plasma torch (at the value of η_pl · η_cs = 0.6) P₂ₚₜ₂, kW</td>
<td>28.33 39.59 17.99 35.21 27.16 32.45♦ 42.22♦ 21.65 18.76♦ 18.72♦</td>
</tr>
<tr>
<td>Enthalpy (MJ/kg) / Temperature (K) for N₂-plasma at plasma torch outlet</td>
<td>13.20 / 6200 18.84 / 6650 9.01 / 5650 17.12 / 6500 13.60 / 6250 14.89♦ / 6500 13.60 / 6250 14.89♦ / 6500 10.84 / 5900 7.44♦ / 3100 (CO₂) 6.56♦ / 3000 (CO₂)</td>
</tr>
<tr>
<td>Enthalpy (MJ/kg) in the flow after the combination of (torch + intensifier) with shroud</td>
<td>2.72 2.75 2.57 3.70 3.57 1.89♦ 1.94♦ 1.63 3.81♦ 4.22♦</td>
</tr>
</tbody>
</table>
Footnote for the Table.
Unit symbols for the parameters:
mass fraction of fuel in the mixture – $\gamma_{hf}$; 
process productivity on final product (i.e. oxide or carbide powder material) – $G_{pr}$; 
the difference between the enthalpies of final ceramic material (as (*) the case of APS-process with Al(OH)$_3$-feedstock was marked, which differs by the taking account of energy consumption for feedstock heating up to its dissociation to oxide) at final temperature $T_f$ and at initial $T_0$ for the reacting mixture – $(H^f_H - H^o_H)$; 
the equivalence ratio for analyzed reacting mixture $ER = (G_{ox}/G_f)/R_{st}$ (where $G_{ox}/G_f$ – ratio of the mass flow rates of oxidizer and fuel for the mixture; $R_{st}$ – ratio of the flow rates of these reagents in the stoichiometric mixture, which is sufficient for complete fuel oxidation); 
energy efficiency for the heating of initial material in the mixture (ignoring the contribution of CPP’ efficiency) – $EnE_2$; 
energy efficiency for the heating of initial material (ignoring the contribution of the fuel enthalpy in the heating process) – $EnE_3$; 
degree of autothermicity of the reacting system on temperature – $AD_T$ (K/K) and on enthalpy – $AD_H$ (J/J); 
effective hydrogen to carbon ratio for initial reacting mixtures with varied chemical composition [33] – $H/C_{eff}$; 
required minimal power of plasma torch (at total energy efficiency of the combination “torch + attached protective “shroud” $\eta_{hs} = 0.6$) – $P_{pt, 2}$.

Symblos:
† – micro-impurity (< 1 % of total mass of condensed products), ♦ – with taking account of effect of heating value (HHV) of fuels in these POA-APS-regimes as for complete combustion.

Results of the modeling. The calculated efficiency parameters for C–H–O–N–Ar–Me systems (Me = Al, Cr, $p = 0.101$ MPa) are shown in Table as for the simulants of operating regimes of the plasma spraying system (APS-process) for oxide and carbide coatings, using proposed fuel intensifier, for two variants on injected fuel evolution: a) regimes with complete oxidation (i.e. combustion) assistance (CA-APS), b) regimes with its partial oxidation assistance (POA-APS). Figures 2–4 represent the examples of data obtained on the compositions during heating of the reacting systems for two variants (CA- and POA-APS) for the cases that simulate thermodynamically optimal conditions for processing regimes with Al$_2$O$_3$ and Cr$_2$C$_2$ (the condensed phases are indicated by the symbol “c” in the graphs). For the cases that are identical to the ones in the Table, but without metals (i.e. C–H–O–N–Ar–system, see their compositions in Figure 5), it was found that for the regime with $ER = 1.0$ (CA-APS-process) temperature $T_{ad} = 1597$ K and at $ER = 0.30$ (POA-APS-process) the value $T_{ad} = 938$ K. Besides, in Figure 6 the dependences for total enthalpies of analyzed C–H–O–N–Ar–Al-, C–H–O–N–Ar–Cr- and C–H–O–Al-systems are presented. The regimes investigated, which simulate the spraying of oxides (on the example of Al$_2$O$_3$ from two kinds of feedstock), surpass (by 5–20 %) on calculated output characteristics, such as energy efficiencies and energy consumption for heating, the conventional method of powder heating during the spraying with N$_2$-plasma (especially, case with Al$_2$O$_3$ powder), as well as one of the new methods with (CO$_2$+CH$_4$)-plasma [5–6, 9], – see the Table for comparison of the regimes: 2 with 3; 4 with 5; 9.

In Figure 7 the comparison of the part of the found efficiency parameters is presented for various cases of the modeled systems as the simulants for regimes of plasma spray with the fuel assistance. It is evidently from the Figure 7 as well as from the results of the Table, that the case of proposed FA-APS
Figure 3. Calculated composition for quasi-equilibrium system C–H–O–N–Ar–Cr at $T = 300–3000$ K ($p = 0.101$ MPa) with the ratios of initial reagents corresponding to the model regime of carbide coating spraying with use of initial $\text{Cr}_3\text{C}_2$ powder in reducing gas medium, which is achievable at the conditions of partial oxidation of LPG (see regime 6 in the Table) at the mixture equivalence ratio $\text{ER} = 0.30$. (In this calculation the absence of CrN and Cr$_2$N phases was specified for kinetic reasons of the initial carbide-contained heterogeneous systems of this group at $T < 1200$ K [4])

Figure 4. Calculated composition for equilibrium system C–H–O–Al at $T = 300–3000$ K ($p = 0.101$ MPa) with the proportion of initial reagents, that is simulating the experiment, which is analogue of our proposed plasma-fuel spray process and was performed by the authors [5] with the effect of complete melting of alumina powder in the DC plasma torch jet in reducing medium in the mixture of $(\text{Al}_2\text{O}_3+\text{CO}_2+\text{CH}_4)$ at the conditions of partial oxidation of the alkane fuel (see regime 10 in the Table).

Figure 5. Composition for equilibrium systems C–H–O–N–Ar (without metals) for the range of 300–6000 K ($p = 0.101$ MPa), with the ratios of initial components corresponding to the regimes, which are applicable for deposition of ceramic coatings: in the oxidizing medium formed by the "$\text{N}_2+\text{air}+\text{LPG fuel}"$-mixture (CA-APS-process) at the equivalence ratio $\text{ER} = 1.00$ and $T_{\text{ad}} = 1597$ K (a), and in the reducing medium formed by the similar mixture (POA-APS-process) at $\text{ER} = 0.30$ and $T_{\text{ad}} = 938$ K (b). For these regimes the nitrogen flow rate $G_{\text{N}_2} = 1.2 \cdot 10^{-3}$ kg/s

Figure 6. Mass averaged enthalpies of the simulated C–H–O–N–Ar–Al-, C–H–O–N–Ar–Cr- and C–H–O–Al-systems at the range of $T = 300–3000$ K ($p = 0.101$ MPa) for the regimes 2 (with Al$_2$O$_3$ feedstock), 4 (with Al(OH)$_3$ feedstock), 7 (with Cr$_3$C$_2$ feedstock) and 9 (with Al$_2$O$_3$ feedstock) in the Table.
with LPG fuel for the heating of ceramic powders (especially, alumina) demonstrates the advantage of this FA-APS (in particular, on the energy efficiencies and total energy consumption $EC$) in a comparison with the “basic” regimes of APS of the powders (in pure $N_2$ plasma).

As a result for the cases of FA-APS with $Al_2O_3$-feedstock and with $Cr_3C_2$ one it was found that it is potentially possible to reach such enhanced level of the process productivity on the final products $G_{pr}$ as close to 17 and 28 kg/h, respectively (at the moderate values of electric energy consumption $EC_e$ – near 1.8 and 1.0 kWh/kg (see the Figure 7, a, d)). For these two powder heating cases the values of the required power of the torch (at $\eta_p = 0.8$) are as the follows: $\geq 28.2$ and $\geq 22.3$ kW.

In accordance with obtained results for the variants of this group systems, it was also found that for the regimes simulating the heating of carbides (in particular, $Cr_3C_2$, – see regime 6 in the Table) in ($N_2$-air-LPG)-mixtures, the parameters of the process efficiency differ slightly from those for the conventional (clear-endothermal) regimes of their processing in $N_2$ (in the spraying UPU-3D units [1, 3]). For the case of processing regimes of $Al(OH)_3$ hydroxide, they are explicitly worse than the CA-APS-variant with $Al_2O_3$-powder feedstock by the level of output efficiency parameters, but nevertheless, this variety of APS with dissociation-able $Al(OH)_3$ feedstock will be quite promising due to very low prices for this material (only 0.6–2.0 US$/kg) [34], in a comparison with commercial $Al_2O_3$ powders for spraying.
Conclusions. 1. The opportunity for upgrading of the industrial-type unit/system of atmospheric pressure for thermal spraying of ceramic powders with DC electric arc torch (30–40 kW power) by use of experimental variant of fuel gas-vortex intensifier was considered.

2. Special analysis of possible parameters of the produced mixed high-enthalpy flow after the plasma torch with this intensifier was performed based on thermodynamic calculations for the cases of C–H–O–N–Ar–Al+, C–H–O–N–Ar–Cr+, and C–H–O–Al-systems in order to assess the potential of this system to modify the technology of oxide and carbide ceramic coatings formation. For the analyzed regimes, simulating spraying of alumina, they are 10–20 % superior in terms of the thermochemical characteristics of process to both the conventional method of powder heating during spraying in N₂, and the new efficient variant under (CO₂+CH₄)-plasma conditions, proposed in recent years.

3. The case of proposed FA-APS with LPG fuel for the heating of ceramic powders (especially, alumina) demonstrates the advantage of this FA-APS (in particular on the energy efficiencies and EC) in a comparison with the “basic” regimes of APS of the powders (in N₂ plasma). For the variants of FA-APS with alumina feedstock and for Cr₃C₂ feedstock powder it was found to be potentially possible to reach (at the moderate values of total electric energy consumption EC for plasma torch and auxiliary equipment, – near 1.8 and 1.0 kWh/(kg of final ceramic product)) such enhanced level of the process productivity on the final product $G_{pr}$ as approximately 17 and 28 kg/h, respectively.

References


