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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 Al_2O_3, Cr_3C_2 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 Al_2O_3 spraying, surpass on calculated energy efficiency characteristics (by 10–20 %) one of the new prospective spraying methods with (CO_2+CH_4)-plasma, as well as the conventional method of powder heating during the spraying with N_2-plasma. The case of our proposed fuel assisted process (FA-APS) with liquefied petroleum gas (LPG) fuel for the heating of ceramic powders (especially, Al_2O_3) 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 N_2 plasma of the standard torch). For the variants of the FA-APS with Al_2O_3 and Cr_3C_2 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: $\geqslant 28.2$ and $\geqslant 22.3$ kW.

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

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ОПРЕДЕЛЕНИЕ ВОЗМОЖНОСТИ МОДЕРНИЗАЦИИ СИСТЕМЫ НА ОСНОВЕ ДУГОВОГО ПЛАЗМОТРОНА ДЛЯ ГАЗОТЕРМИЧЕСКОГО НАПЫЛЕНИЯ КЕРАМИЧЕСКИХ МАТЕРИАЛОВ С ИСПОЛЬЗОВАНИЕМ ТОПЛИВНОГО ВИХРЕВОГО ИНТЕНСИФИКАТОРА.
ЧАСТЬ I: ТЕРМОДИНАМИЧЕСКОЕ МОДЕЛИРОВАНИЕ ПАРАМЕТРОВ ЭФФЕКТИВНОСТИ СИСТЕМЫ

Аннотация. Одно из перспективных направлений в технологиях газотермического, в том числе плазменного, напыления функциональных керамических покрытий, – это разработка новых их вариантов, с применением ввода в теплоноситель недорогих смесей промышленных углеводородов с окислителем для снижения энергоемкости

процесса. Такую плазменно-топливную разновидность наиболее перспективно использовать для получения тугоплавких функциональных покрытий. Для этой цели нами рассмотрена возможность модернизации промышленной системы для напыления керамических порошковых материалов на основе дугового плазмотрона на 25–40 кВт путем использования пробного варианта топливного газо-вихревого интенсификатора. При этом был проведен термодинамический анализ систем С–Н–О–N–Ar–Me (Me = Al, Cr) и С–Н–О–Al с целью моделирования возможных параметров генерируемой высокотемпературной струи после плазмотрона с данным интенсификатором для определения применимости такой системы для формирования оксидных и карбидных покрытий (на примере нескольких порошковых материалов, в том числе Al_2O_3, Cr_3C_2). Изученные нами новые режимы-имитаторы напыления оксида алюминия по расчетным параметрам энергоэффективности на 10–20 % превосходят как традиционный способ нагрева порошков при напылении (в N_2-плазме), так и современный, разработанный в ряде исследований способ напыления в условиях смесевой (CO_2+CH_4)-плазмы. Показано, что предложенный вариант для модернизации процесса напыления с использованием промышленного пропан-бутанового топлива (сжиженного газа) позволяет в термодинамически равновесных условиях получить небольшое преимущество, по сравнению с традиционным плазменным напылением, при нагреве и плавлении керамических материалов (в особенности, Al_2O_3) по таким параметрам, как удельные энергозатраты и энергетические КПД процесса. Также установлено, что для расчетных случаев систем с оксидноалюминиевым и с карбиднохромовым порошками (сырьем) потенциально возможная производительность процесса по нагреваемым до плавления порошкам составляет соответственно 17 и 28 кг/ч при общих удельных энергозатратах *EC* не выше, чем 1,8 и 1,0 кВтч/(кг продукта) и при требуемой мощности плазмотрона $\geqslant$ 28,2 и $\geqslant$ 22,3 кВт для нагрева этих двух вариантов сырьевых порошков.

Ключевые слова: дуговой плазмотрон, ассистируемое горением плазменное напыление, порошки, оксиды, карбиды, термодинамика, энергетический КПД, энергозатраты

Introduction and research task. One of the most used industrial techniques for coatings formation for various functional purposes is a method of thermal spraying, which provides enhancement of wear-, thermal and corrosion resistance of the surfaces of machine parts and equipment. The world market for equipment and technologies for thermal spraying reached at 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 Al_2O_3 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 kWh 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 for melting/spheroidizing of ceramic (Al_2O_3, ZrO_2, TiO_2, rare earth oxides, WC) and metal (copper alloys for antibacterial coatings, heat-resistant nickel alloys) powder materials, as with the use of hydrocarbon based heat-transport gases (including CH_4 + CO_2 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 alkane hydrocarbons (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_2O_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 + (air + 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.
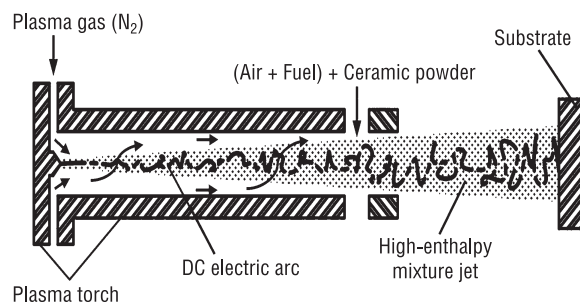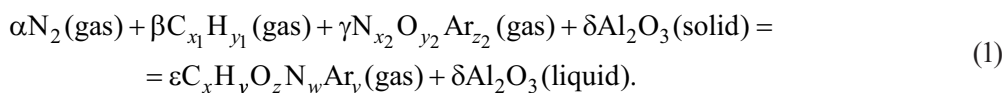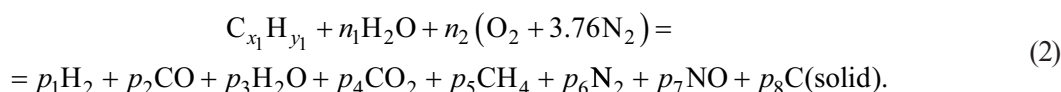

Figure 1. Schematic diagram of the analyzed processing system with ceramic powder injection, using fuel-assisted process for technology of thermal plasma spraying (APS) for oxide and carbide coatings formation

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_2O_3) and carbide (Cr_3C_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):

$$\alpha N_2(gas) + \beta C_{x_1}H_{y_1}(gas) + \gamma N_{x_2}O_{y_2}Ar_{z_2}(gas) + \delta Al_2O_3(solid) =$$
$$= \varepsilon C_x H_y O_z N_w Ar_v(gas) + \delta Al_2O_3(liquid). \tag{1}$$

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:

$$C_{x_1}H_{y_1} + n_1 H_2O + n_2 (O_2 + 3.76 N_2) =$$
$$= p_1 H_2 + p_2 CO + p_3 H_2O + p_4 CO_2 + p_5 CH_4 + p_6 N_2 + p_7 NO + p_8 C(\text{solid}). \tag{2}$$

The composition of selected fuel (LPG) was taken for further calculation based on the experimental data [16] for this feedstock: CH_4 – 0.6; C_2H_6 – 5.6; C_3H_8 – 72.5; n-butane C_4H_{10} – 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 $C_xH_yO_zN_wAr_vMe_k$ can be expressed as follows: $x = \beta \cdot x_1$, $y = \beta \cdot y_1$, $z = (\gamma \cdot y_2 + 3\delta)$, $w = (2\alpha + \gamma \cdot x_2)$, $v = \gamma \cdot z_2$, $k = 2\delta$ (for systems with Al_2O_3); and $x = (\beta \cdot x_1 + 2\delta)$, $y = \beta \cdot y_1$, $z = \gamma \cdot y_2$, $w = (2\alpha + \gamma \cdot x_2)$, $v = \gamma \cdot z_2$, $k = 3\delta$ (for systems with Cr_3C_2).

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-ash 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 EnE_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 $\Delta H_{MeO_x} = \left(H_{T_3} - H_{298} \right)_{MeO_x}$, 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:

$$EnE_1 = \frac{G_{MeO_x} \Delta H_{MeO_x}}{\left(G_f LHV_f \right) + \left[P_{pt} / (\eta_{el}\eta_{pt}) \right] + \left[\left(\sum_k N_{(aeq)k} \right) / \eta_{el} \right]}. \tag{3}$$

Here G_{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_{aeq} 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), η_{pt} is thermal efficiency of the torch (assumed equal to 0.80 based on aggregated data for non-transferred arc plasma torches [25]), η_{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 (ΔH_{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 EnE_2 (which differs from 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 EnE_2), and the energy efficiency of EnE_3 (calculated, in a contrast with EnE_1, without taking into account the effect of fuel enthalpy on the last efficiency, i.e. with $G_f \cdot LHV_f = 0$). 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 kW·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 consideration (excluding the contribution of the CPP efficiency) was calculated as $EC = (P_{pl}/\eta_{pt} + \sum N_{aeq})/G_{MeOx}$; and the degree of overheating (J/J) of the reacting system beyond T_2 (i.e., to the desired specified temperature of the process T_3) as: $DOH = (I_{pr}(T_2) - I_{pr}(T_0))/(I_{pr}(T_1) - I_{pr}(T_0))$. Here, $I_{pr}(T)$ denotes three variants of the sum of enthalpies of the equilibrium products of interaction (taking into account their molar fractions M_i in the reacting mixture): at high temperatures T_2 and T_3, and at initial $T_0 = 298.15$ 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:

$$N_0 = Q_{hm} + Q_w + Q_{ex} = \left(\Delta H_1^m + \Delta H_2^m + \Delta H_3^m + \Delta H_4^m + \Delta H_5^m \right) + Q_w + Q_{ex}. \tag{4}$$

Here in the considered general case of this air-plasma APS-process (in which, as an option, heating of the powder of thermally dissociating feedstock/material is allowed), the total temperature range for the sprayed substance (which, for the case, e.g. of obtaining a coating from Al_2O_3 with estimated value of melting point of 2328 K [27], ranges approximately from 298.15 to 2500 K) is divided to the regions: 1) from $T_0 = 298.15$ K to the temperature of feedstock decomposition (to final oxide), equal to T_1; 2) from T_1 to melting point of oxide particles T_2; 3) from T_2 to the maximum temperature T_3 reached by molten particles in front of metal substrate. In the equation (4), for the process thermochemical zone (including quasi-cylindrical section between the outlet from the torch anode and the substrate), the following unit symbols are used: total thermal power (in W) of the feedstock and the heat-transport gas at the inlet to the zone under consideration: $N_0 = Q_{hc} + N_{hm} = Q_{hc} + \sum_j (M_j H_j)$ (where Q_{hc} is the thermal power of

the material (if it is injected as preheated one), N_{hm} is the thermal power of the heat transport gas, i.e. plasma gas, preheated by the torch arc); Q_{hm} – "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 dissociation, as, e.g. in the techniques of special APS-, SPS-, SolPS-spraying [9, 14, 30]); Q_w – heat losses from gas-powder flow in the considered zone in radial direction to surrounding air or to the walls of the protective channel (in the case of flow inside the channel (e.g. shroud, as it was in the oxy-fuel spraying [31])); Q_{ex} is the heat power of the gas phase of this high-enthalpy jet at the exit from the considered zone after the end of powder melting, which decreases during the following heat transfer with substrate; $\Delta H_1^m = (H_{T_1}^0 - H_{T_0}^0)_{hm}$, is the difference between the enthalpy of the initial material (undissociated) at T_1 (e.g., for the case of $Al(OH)_3$ equal to ~ 550 K [32]) and its enthalpy at T_0; $\Delta H_2^m = \Delta H_{dr298}^0$ is the heat of dissociation reaction (endothermic) of the initial feedstock powder (e.g. with the formation of oxide) at T_1; $\Delta H_3^m = (H_{T_2}^0 - H_{T_1}^0)_{hm}$ is the difference between the enthalpy of dissociated powder at the T_2 and its enthalpy at T_1; $\Delta H_4^m = (\Delta_f H_{liquid}^0 - \Delta_f H_{solid}^0) = \Delta H_{melt}^0$ – is the heat (normalized to the standard conditions) of powder melting at T_2; $\Delta H_5^m = (H_{T_3}^0 - H_{T_2}^0)_{hm}$ is the difference between the enthalpy of final powder at T_3, slightly higher (usually, for technological reasons, by 150–300 K) the T_2, 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

Parameter	1 – Al_2O_3	2 – Al_2O_3	3(bas) – Al_2O_3	4 – $Al(OH)_3$	5 (bas) – $Al(OH)_3$	6 – Cr_3C_2	7 – Cr_3C_2	8 (bas) – Cr_3C_2	9 – Al_2O_3 (analog 1 on [5])	10 – Al_2O_3 (analog 2 on [5])
					Initial parameters					
Type of operating gas / flow rate of gas for arc stabilization in the torch (g/s) / use of fuel in the initial mixture	Air+ N_2 / 1.20 (N_2)/ LPG	the same that #1	N_2 / 1.20 / –	the same that #1	the same that #3	the same that #1	the same that #1	the same that #3	CO_2 / 1.20 / CH_4	CO_2 / 1.20 / CH_4
Fraction of initial powder in the mixture γ_{fm}, kg/kg	0.500	0.620	0.620	0.650	0.650	0.800	0.800	0.800	0.620	0.620
Fraction of final product in the product mixture at T_3 γ_{pr}, kg/kg	0.500	0.620	0.620	0.425	0.425	0.800	0.800	0.800	0.620	0.620
Fraction of fuel in the mixture γ_{hf}	0.017	0.013	0	0.011	0	0.013	0.011	0	0.047	0.064
Melting point of the product T_2, K	2328	2328	2328	2328	2328	2108	2108	2108	2328	2328
Desired specified temperature T_3, K	2500	2500	2500	2500	2500	2300	2300	2300	2500	2500
$H^0_{T3} - H^0_{298}$, MJ/(kg of final powder)	3.37	3.37	3.37	5.82*	5.82*	1.71	1.71	1.71	3.37	3.37
Oxidizer – fuel equivalence ratio ER [21]	1.050	1.050	0	0.500	0	0.300	0.500	0	0	0
					Output parameters					
Process productivity on final product G_{pr}, kg/h	10.17	16.60	7.04	7.12	5.24	27.85	33.65	17.26	8.026	8.463
Condensed products in the reacting system at T_2 and T_3 temperatures	Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3	Cr_3C_2	Cr_3C_2, Cr_7C_3	Cr_3C_2, C(s) †	Al_2O_3	Al_2O_3
Adiabatic temperature of the system T_{ad}, K	986	837	298	365	300	699	827	275	370	375
Degree of overheating (DOH) of the system beyond T_2, J/J	1.100	1.095	1.080	1.098	1.106	1.110	1.106	1.117	1.066	1.064
Energy efficiency of process EnE_1, J/J	0.167	0.197	0.175	0.158	0.154	0.172	0.179	0.183	0.114	0.102
Energy efficiency of process EnE_2, J/J	0.381	0.461	0.446	0.385	0.391	0.390	0.413	0.467	0.242	0.209
Energy efficiency of process EnE_3, J/J	0.181	0.208	0.175	0.164	0.154	0.186	0.192	0.183	0.130	0.121
Energy consumption EC, kW·h/kg of product	2.037	1.772	2.101	3.888	4.136	1.000	0.969	1.015	2.831	3.045
Degree of autothermicity AD_{T3}, K/K	0.312	0.245	0	0.030	0	0.200	0.264	0	0.033	0.035
Degree of autothermicity AD_{H3}, J/J	0.249	0.180	0	0.083	0	0.130	0.174	0	0.079	0.098
Ratio (H/C_{eff}) for the initial mixture	−109.5	−125.9	0	−131.13	0	−3.68	−3.78	0	−5.257	−4.409
Required minimal power of plasma torch (at its efficiency $\eta_{pl} = 0.8$) P_{pt_1}, kW	19.78	28.23	13.49	25.64	20.37	22.31◆	29.64◆	16.24	11.15◆	9.83◆
Required minimal power of plasma torch (at the value of $\eta_{pl}\cdot\eta_{cs} = 0.6$) P_{pt_2}, kW	28.33	39.59	17.99	35.21	27.16	32.45◆	42.22◆	21.65	18.76◆	18.72◆
Enthalpy (MJ/kg) / Temperature (K) for N_2-plasma at plasma torch outlet	13.20 / 6200	18.84 / 6650	9.01 / 5650	17.12 / 6500	13.60 / 6250	14.89 / 6350	19.78 / 6700	10.84 / 5900	7.44◆ /3100 (CO_2)	6.56◆ /3000 (CO_2)
Enthalpy (MJ/kg) in the flow after the combination of (torch + intensifier) with shroud	2.72	2.75	2.57	3.70	3.57	1.89◆	1.94◆	1.63	3.81◆	4.22◆

Footnote for the Table.

Unit symbols for the parameters:

mass fraction of fuel in the mixture – γ_{hf};

process productivity on final product (i.e. oxide or carbide powder material) – G_{pr};

mass fraction of final product/material in the product mixture at T_3 – γ_{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_3 and at initial T_0 for the reacting mixture – $(H_{T3}^0 - H_{298}^0)$;

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" $\eta_{pl} \cdot \eta_{cs} = 0.6$) – P_{pt_2};

Symbols:

† – 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$_3$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
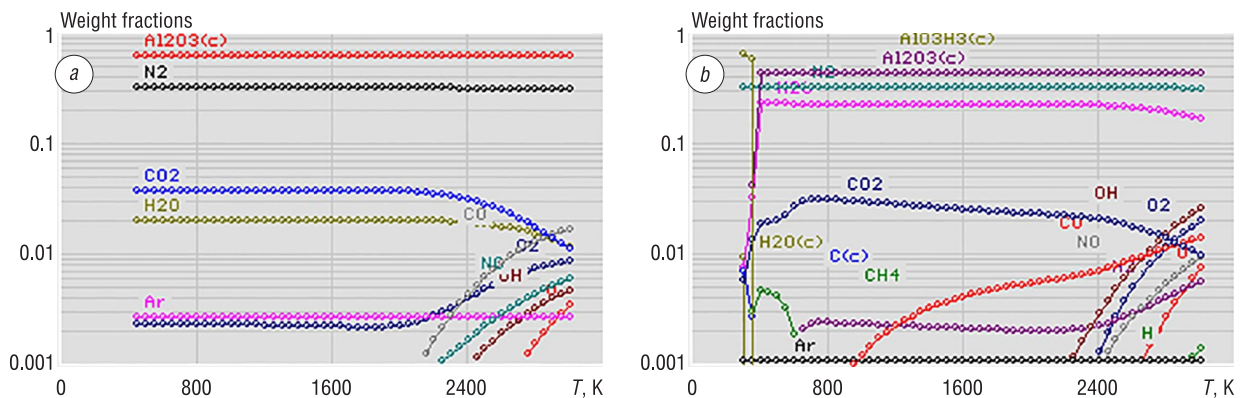

Figure 2. Calculated chemical compositions for equilibrium systems C–H–O–N–Ar–Al at T = 300–3000 K (p = 0.101 MPa) with the ratios of initial reagents corresponding to model regimes of alumina coating spraying with use of initial Al$_2$O$_3$ powder (*a*) in oxidative gas medium at the equivalence ratio ER = 1.05 (see regime 2 in the Table), and with initial Al(OH)$_3$ feedstock powder (*b*) in combined reducing-oxidative medium at ER = 0.50 (see regime 4 in the Table)
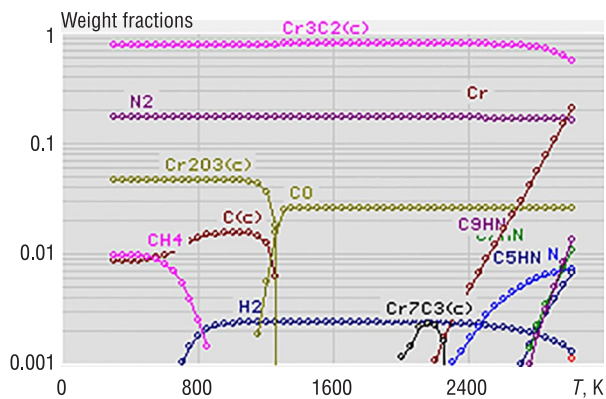
Figure 3. Calculated composition for quasi-equilibrium system C–H–O–N–Ar–Cr at T = 300–3000 K (p = 0.101 MPa) with the ratios of initial reagents corresponding to the model regime of carbide coating spraying with use of initial Cr_3C_2 powder in reducing gas medium, which is achievable at the conditions of partial oxidation of LPG (see regime 6 in the Table) at the mixture equivalence ratio ER = 0.30. (In this calculation the absence of CrN and Cr_2N phases was specified for kinetic reasons of the initial carbide-contained heterogeneous systems of this group at $T \leqslant 1200$ K [4])
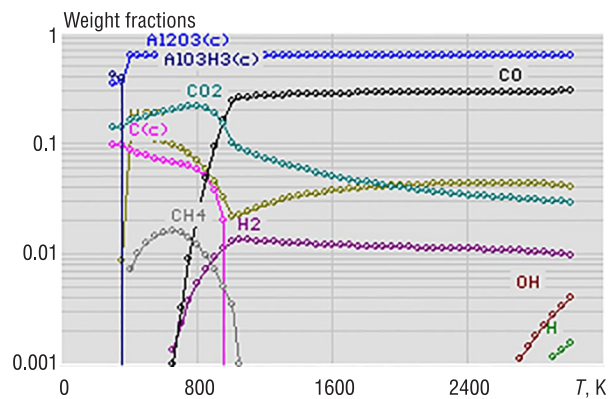
Figure 4. Calculated composition for equilibrium system C–H–O–Al at T = 300–3000 K (p = 0.101 MPa) with the proportion of initial reagents, that is simulating the experiment, which is analogue of our proposed plasma-fuel spray process and was performed by the authors [5] with the effect of complete melting of alumina powder in the DC plasma torch jet in reducing medium in the mixture of $(Al_2O_3+CO_2+CH_4)$ at the conditions of partial oxidation of the alkane fuel (see regime 10 in the Table)
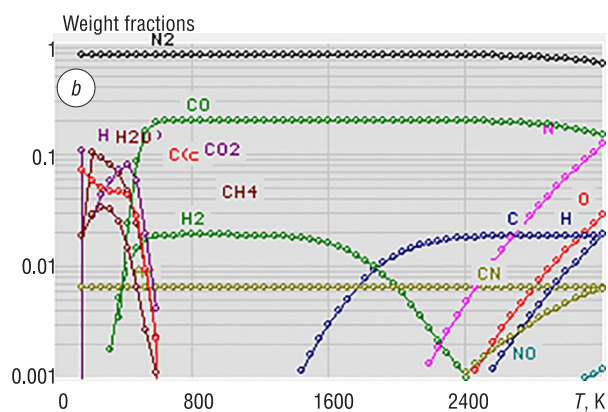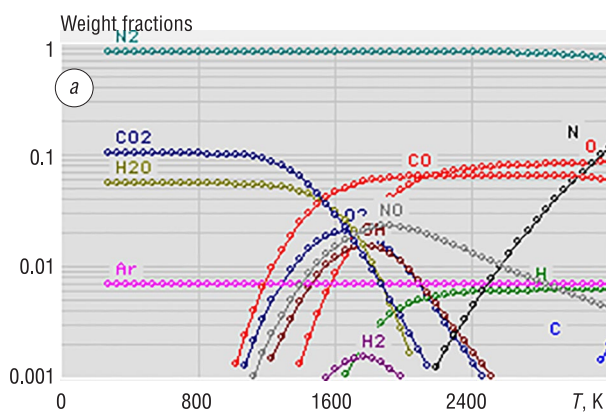

Figure 5. Composition for equilibrium systems C–H–O–N–Ar (without metals) for the range of 300–6000 K (p = 0.101 MPa), with the ratios of initial components corresponding to the regimes, which are applicable for deposition of ceramic coatings: in the oxidizing medium formed by the "N_2 +air + LPG fuel"-mixture (CA-APS-process) at the equivalence ratio ER = 1.00 and T_{ad} = 1597 K (a), and in the reducing medium formed by the similar mixture (POA-APS-process) at ER = 0.30 and T_{ad} = 938 K (b). For these regimes the nitrogen flow rate G_{N2} = 1.2·10^{-3} kg/s

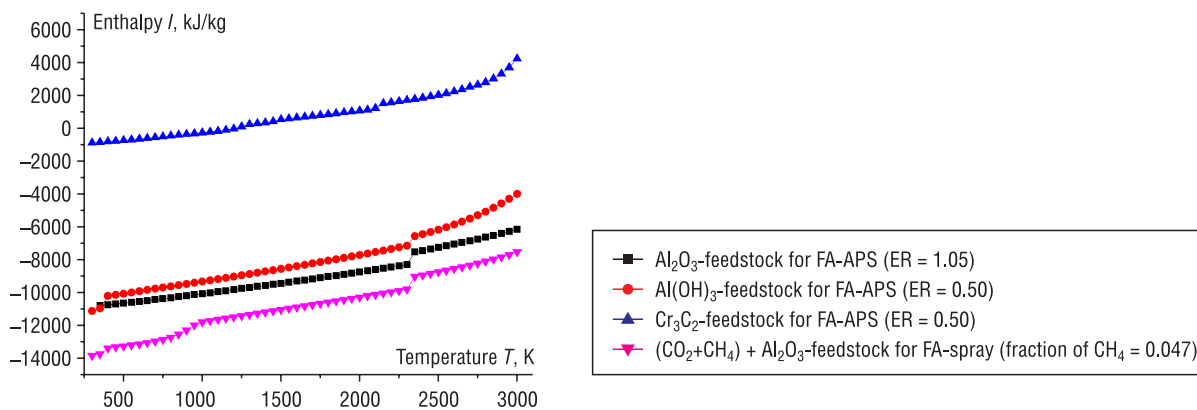
Figure 6. Mass averaged enthalpies of the simulated C–H–O–N–Ar–Al-, C–H–O–N–Ar–Cr- and C–H–O–Al-systems at the range of T = 300–3000 K (p = 0.101 MPa) for the regimes 2 (with Al_2O_3 feedstock), 4 (with $Al(OH)_3$ feedstock), 7 (with Cr_3C_2 feedstock) and 9 (with Al_2O_3 feedstock) in the Table

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, – 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 $\eta_{pl} = 0.8$) are as the follows: $\geqslant 28.2$ and $\geqslant 22.3$ kW.
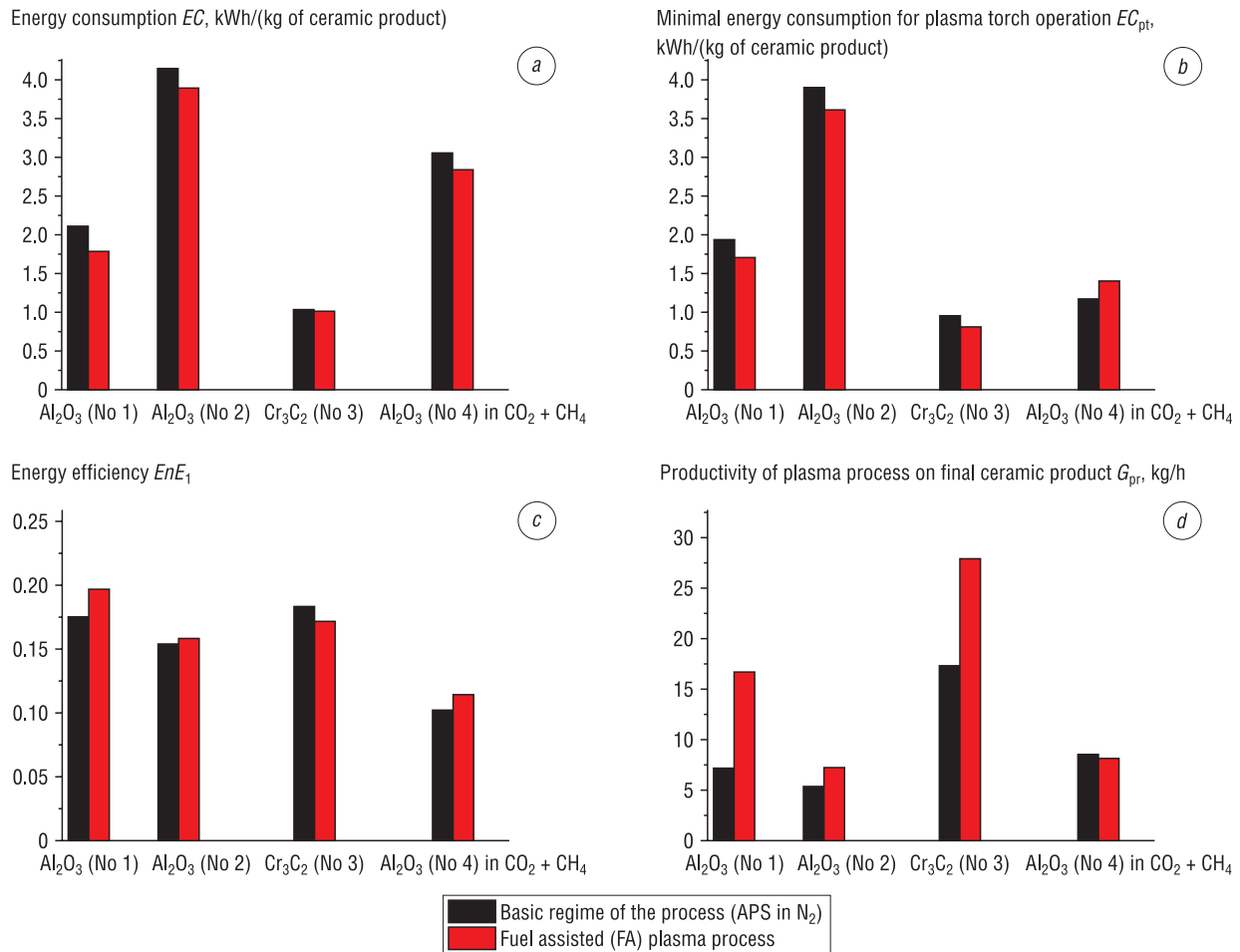

Figure 7. Comparison of efficiency parameters for various cases of modeled C–H–O–N–Ar–Me- and C–H–O–Al-systems: a – comparison for energy consumption EC; b – comparison for energy consumption for plasma torch operation (ignoring the CPP' efficiency and with taking account of effect of HHV of fuel in POA-APS-regimes as for combustion) EC_{pt}; c – comparison for EnE_1; d – comparison for the process productivity on the product. Here the red columns correspond to the following regimes in the Table: 1 – CA-APS with Al_2O_3-feedstock (regime 2), 2 – POA-APS with $Al(OH)_3$-feedstock (regime 4), 3 – POA-APS with Cr_3C_2-feedstock (regime 6), 4 – FA-spray with Al_2O_3 in (CO_2+CH_4)-gas (regime 9); and the black columns correspond to the "basic" regimes of APS (with pure N_2 medium – 3, 5, 8) and for regime 10 for the mixture of $(Al_2O_3+CO_2+CH_4)$

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 N_2, and the new efficient variant under (CO_2+CH_4)-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 N_2 plasma). For the variants of FA-APS with alumina feedstock and for Cr_3C_2 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.

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