Advanced oxide powders processing based on cascade plasma

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Abstract. Analysis of the potential advantages offered to thermal spraying and powder processing by the implementation of plasma torches with inter-electrode insert (IEI) or, in other words, cascade plasma torches (CPTs) is presented. The paper provides evidence that the modular designed single cathode CPT helps eliminate the following major disadvantages of conventional plasma torches: plasma parameters drifting, 1-5 kHz pulsing of plasma flow, as well as excessive erosion of electrodes. More stable plasma results in higher quality, homogeneity and reproducibility of plasma sprayed coatings and powders treated. In addition, CPT offers an extremely wide operating window, which allows better control of plasma parameters, particle dwell time and, consequently, particle temperature and velocity within a wide range by generating high enthalpy quasi-laminar plasmas, medium enthalpy transient plasmas, as well as relatively low enthalpy turbulent plasmas. Stable operation, flexibility with plasma gases as well as wide operating window of CPT should help significantly improve the existing plasma spraying processes and coatings, and also help develop new advanced technologies.

1. Introduction
Knowledge of the fundamental physical processes, taking place in the linear direct current (DC) plasma torches, allowed to suggest a simple classification and to reduce multiple constructive solutions to three principal classes of torches [1, 2] (see figure 1).

The first torch class is widely used in the industry and in scientific works. This torch is equipped with tube exit electrode and has a self-installing length of the arc [1, 2]. Volt-Ampere characteristics (VACs) of such plasma torches have a falling nature (figure 1, curve 1). The mean arc length $l_a$ is a function of arc current, chamber diameter, gas flow rate and pressure. It further depends on the type of working gas and on polarity of the exit electrode. A large-scale shunting, taking place in the transient zone of the discharge channel, forms the mechanism for arc length changes.

The second class of the plasma guns is characterised by the fact that the average arc length $l_a$ is constant in sufficiently wide range of current changes ($I_e<I<I_1$) while other above-mentioned parameters are constant. The arc length $l_a$ is always less than the length of the self-installing arc $l_e<l_i$ within the first torch class. VAC has a $U$-shape form (figure 1, curve 2). Without taking special measures value $U$ is limited to the value where VAC curves 1 and 2 intercept. There are several technical solutions, providing the constant average length of the arc. One of them is the use of a backward-facing stepped anode [1. 2]. The peculiarities of flow gasdynamic structure inside the backward-facing stepped electrode, that consists of two cylinders with different diameters, the diameter of the exit part of the electrode $d_3$ being larger than $d_2$, have been analyzed in [2, 3]. It was mentioned that in this case VAC of the arc is situated below VAC of the arc with self-installing mean length. The plasma torches of second type are working stable without additional resistance in the circuit on an upward going branch of arc VAC.
Figure 1 Classification of the linear type DC torches. VACs correspond to three classes of torches. I – torches with self-installing length of arc, II – torches with length of arc fixed by a backward-facing stepped anode, III – cascade plasma torches. Dash line corresponds to fixed electric power of torches (P=const).

During the last decades a great attention is paid to the third type of the non-transferred arc torches, in which the averaged arc length in non-changeable, but longer than that of the self-installing length of arc [1, 2]. VAC of this arc (figure 1, curve 3) is situated higher than the two previously mentioned cases. The increase of the average length of the arc is achieved by IEI placed between the anode and the cathode, the length of which is larger than lsi. The insert may be solid, porous, with any gas injection through porous structure or sectional with/without gas injection into intersection gaps. This type of torch will be referred to as cascade torch/gun.

Below is a brief overview of the research and development, carried out in the Khristianovich Institute of Theoretical and Applied Mechanics SB RAS, illustrating the possibilities of cascade torches in context of elaboration of high-tech processes of plasma spraying and powder treatment.

2. Demands on torches for plasma spraying and powders processing
Requirements to a hypothetical “ideal” torch could be used as a set of criteria to compare different possible designs of plasma guns and to make a decision regarding the future of a plasma product line.

In this connection, the following main requirements could be formulated:

- high quality consistent and reproducible sprayed coatings and powders, in particular, hollow microspheres;
- high efficiency and low cost process;
- wide operational window for spraying of different materials and low dependence on some unavoidable changes of parameters (for example, independent of spraying distance changes in a case of parts with a complicated shape);
- possibility to get a high productivity, for instance, deposition rate;
- low maintenance, high reliability, user-friendly;
- controllable within a wide plasma jet temperature and velocity range (to control dwell time, particle temperature and aggregate state) with possibility to provide different regimes of plasma jet flow (quasi-laminar, transient and turbulent);
- axially symmetric with the uniform distributions of plasma velocity and temperature;
- minimized pulsations of arc voltage and plasma jet thermal power;
- possibility to use relatively large inner diameter of nozzle and forming nozzle to allow the following: (i) easier arrangement of several powder injectors to control a foot print and/or increase homogeneity of powder treatment due to decrease of the velocity and temperature gradients in the cross-sections of the plasma jet, (ii) low dependence on spray distance...
changes, carrier gas flow variations and powder injection conditions due to decreased sensitivity to particle trajectory;

- long lifetime of the electrodes (no contamination of coatings and powders by electrode material: W, Cu etc.);
- possibility to scale up the design within a wide range, if necessary (different applications and production rates need different power level);
- possibility to use different gases and their mixtures, in particular inexpensive gases, as plasma-forming gases.

3. Background

The following main designs are available now on the marketplace:

- Conventional Metco torches (9MB, F4,…);
- Mettech 100 kW Axial III gun with an axial powder injection;
- Water-stabilized plasma guns;
- PlazJet;
- Triplex 50 kW (Metco).

The analysis showed that none of the designs could satisfy all requirements to the “ideal” gun. The analysis also showed that a “cascade” approach is the most promising from a theoretical standpoint to satisfy the requirements.

The disadvantages of the torches with self-installing length of arc are studied during last two decades. The main of them are the following:

1) the low-frequency pulsations of the arc voltage, i.e. fluctuation of the thermal power of flowing out plasma jet, due to arc length variation and the movement of anode spot attachment conditioned by magnetic and gas dynamic interaction of a radial arm of the arc with a cold wall boundary layer [1, 3, 4]. This results in a considerable inhomogeneity of powder material processing [4, 5];

2) absence of axial symmetry of velocity and temperature fields in flowing out plasma jet and, as consequence, non-uniform heating and acceleration of particles in the cross-section of the jet; the latter causes the absence of axial symmetry of particles’ parameter distributions within a spraying spot.

Discussion regarding the other disadvantages of the conventional DC plasma torches can be found in the publications [4, 5], etc.

4. Features and advantages of the “Cascade” design

A major contribution to study and developing the cascade plasma torches has been made by Zhukov and colleagues [1-3], etc. Results of the investigations and developments of the cascade plasma torches as applied to plasma spraying and powder materials processing have been published in [6-9]. Without going into details, below a brief overview of principal results will be given with the focus on the above-mentioned requirements for the “ideal” torch.

Electrically insulated inter-electrode inserts are applied in the cascade torch (figure 2) to extend and stabilize the arc length over a wide range of gas mass flow rates. Inter-electrode inserts or the neutral electrodes are intermediate electrodes between the cathode and the anode.

A long, high-voltage arc column is stabilized by these neutral inserts rather than by high gas flow rate resulting in more stable plasma jet with minimized pulsation, higher thermal efficiency and, consequently, more efficient particle heating. The concept of low-current and relatively high-voltage design also provides lower cathode and anode erosion [1, 2], longer service life and minimized or no contamination of coating and powder by products of electrodes’ erosion.

The following main advantages for the cascade approach could be formulated more specifically.

1. Significantly lower level of electric power low-frequency pulsations because of the “neutral” electrode with a fixed length (see figures 3a, b). It should result in better coating quality as there is less unmelted particles, better coating homogeneity and deposition efficiency;

2. Very low or no voltage drifting (figure 3c). It results in consistent coating quality and deposition efficiency.
3. Relatively low arc current at fixed electric power (see figure 1) results in a low level of electrodes’ erosion because of the actual heat fluxes into electrodes mainly depend on the arc current. Therefore, the gun should have low maintenance and coatings should not be contaminated by products of erosion (Cu, W, etc.). Cleaner coating results in better quality.

![Image](3. Relatively low arc current at fixed electric power (see figure 1) results in a low level of electrodes’ erosion because of the actual heat fluxes into electrodes mainly depend on the arc current. Therefore, the gun should have low maintenance and coatings should not be contaminated by products of erosion (Cu, W, etc.). Cleaner coating results in better quality.)

4. The “cascade” approach allows changing plasma gases mass flow rate (i.e. Reynolds number, \( \text{Re} = 4G/\pi d_a \mu \)) where \( G \) is the mass flow rate of the working gas, \( d_a \) is the inner diameter of the outlet electrode (anode), and \( \mu \) is the mean-mass dynamic viscosity of the working gas at the exit cross-section of the outlet electrode) within relatively wide range without significant plasma voltage changes (see figure 3). Therefore, plasma temperature, specific enthalpy and velocity could be changed within a wide range, thus increasing the operational window (figure 4). It could create some new technological opportunities.

5. The “cascade” designs have higher thermal efficiency [1]: 60-70% and more vs. 40-60%. Therefore, for the same power level temperature and specific enthalpy of the plasma jet should be higher.

6. The “cascade” approach allows to use more than one swirl (for example, double swirl, first one – between cathode and pilot section, and second one – between pilot section and inter-electrode insert; the second swirl flow can be concurrent or cross-current to the first one. Therefore, relatively wide range of electric force, arc voltage, turbulence number and more spatially uniform plasma temperature, specific enthalpy and velocity distributions could be achieved [2, 3] (see figures 5 and 6, taken from [1,3]). The uniform plasma plume will result in more reproducible powder treatment, higher coating quality and higher deposition efficiency. In accordance with [1,3], the following designations are used in figures 5 and 6: \( d \) – diameter of channel, m; \( I \) – arc current, A; \( G \) – total mass flow rate of plasma-forming gas, kg/s; \( m_s = g_1/g_2 \) – ratio of the mass flow rate of gas supplied between the cathode and pilot section to mass flow rate of gas supplied between the pilot section and inter-electrode insert (position \( \bar{z}_s = z_s/d \) is marked by arrow); \( g_2 \) – mass flow rate of gas supplied between sections of the inter-electrode insert, kg/s; \( p \) – pressure inside the channel, Pa; \( \bar{I} = I/d \) – relative length of the electric-discharge channel; \( \bar{a} = a/d \) – relative length of the inter-electrode insert; \( \bar{z} = z/d \) – non-dimensional axial coordinate.

7. Low current gives possibility to use low cost, high enthalpy gas mixtures like air + natural gas or \( \text{CO}_2 + \) natural gas or other combustible gases. These options could be attractive for the following: 1) low cost manufacturing of micro-spherical, in particular HOSP, powders or other powders where plasma treatment has to be involved, 2) implementation of plasma technologies in countries or areas where high purity inert gases are not available or extremely expensive, 3) air or \( \text{CO}_2 \) mixtures with
different amounts of combustible gases allow to create oxidizing, reducing or neutral atmospheres that could result in some technological advantages. For example, chrome oxide coatings sprayed by Ar/H₂ or N₂/H₂ mixtures could have some inclusions of metallic Cr. This disadvantage could be avoided by application of “oxidizing” plasma.

Figure 4 Operation window of 50-kW cascade torch vs. some commercial torches.

Figure 5 Distributions of the electric field strength (E) – (a), (b), and turbulent number (ε) – (c), along the discharge chamber axis at different conditions of plasma gas (air) supply. (a) – single supply of swirl working gas between the cathode and pilot section; 1, 2 and 3 correspond to initial, transient and turbulent section of the arc, respectively. (b) – distributed supply of air along the channel. \(d = 2 \times 10^{-2} \) m; \(I = 100 \) A; \(I\): \(g_i = 0\), \(G = 24.6 \times 10^{-3} \) kg/s; 1 – \(m_i = 1\); 2 – \(m_i = 1.1\); \(II\): \(g_i = 0.4 \times 10^{-3} \) kg/s, \(G = 28 \times 10^{-3} \) kg/s; 3÷5 – \(m_i = 1.1\); 1.43; 1.65. Dashed line was computed from the following formula, generalizing the experiments

\[ E_r \cdot d = 115(I/d)^{0.23} (G/d)^{0.47} (pd)^{0.2} \]

(c) – distribution of turbulence scale \(ε\) along the channel centerline \((d = 10^{-2} \) m; \(G = 5 \times 10^{-3} \) kg/s). 1 – channel with smooth wall, \(\bar{I} = I/d = 77\); 2-4 – divided channel, \(\bar{a} = a/d = 32\) (2 – \(g_i = 0\); 3 – \(g_i = 0.5 \times 10^{-3} \) kg/s; 4 – \(m_i = 1\) in the cross-section \(\bar{z}_s = 4.3\)); \(I – g_i = 0\); \(II – g_i = 1 \times 10^{-3} \) kg/s.
Figure 6 Distributions of the electric field strength ($E$) along the axis of the electric-discharge chamber at different conditions of plasma gas (air) supply. (a) – cocurrent swirl of gas supplied between pilot and first inter-electrode sections. $d=2\cdot10^{-2}$ m, $\alpha=21.5$; $z_i=3.2$, $I=120$ A, $G=30\cdot10^{-3}$ kg/s, $g_i=0.5\cdot10^{-3}$ kg/s, $g_i+g_2=\text{const}=15\cdot10^{-3}$ kg/s, $1+5-m_s=0.08$; 0.18; 0.39; 0.62 and 1.2, respectively. (b) – cross-current swirl of gas supplied between pilot and first inter-electrode sections. 1 – 4: $m_s=0.08$; 0.37; 1.1 and 2.1; $\xi=5$. (c) – with and without swirl of gas supplied between pilot and first inter-electrode sections. $d=15\cdot10^{-3}$ m; $g_i=1.5\cdot10^{-3}$ kg/s; $G=17.9\cdot10^{-3}$ kg/s, $I=120$ A. 1, 2 – concurrent swirl; 3 – without swirl.

8. High enthalpy plasma gas mixtures result in a longer plasma plume in comparison with Ar based mixtures. Longer plume results in higher “useful” dwell time and possibility to improve heat treatment of sprayed or treated particles. Besides, “long plume” plasma spraying is more forgivable to spraying distance changes that should be important for the product line.

9. The “cascade” design could be scaled up for a wide range of power levels without big problems [9]. It means that the same approach could be used, for example, for 10-30, 30-75, 75-120 kW, etc.

10. The “cascade” design allows realization of both options: sub-sonic and supersonic plasma velocities.

11. Possibility of quasi-laminar and transition plasma flows. These options allow increasing the particles dwell time and, consequently, efficiency of heat transfer from plasma to particles and treated surface [7, 8] (see figures 7, 8 and 9).

Figure 7 Fracture surface of alumina coatings sprayed in turbulent – (a), and quasi-laminar – (b), plasma jet outflow; (c) – experimental data characterizing a bond strength of $\alpha$-$\text{Al}_2\text{O}_3$ coatings sprayed on the stainless steel substrates at different air plasma jet outflow: quasi-laminar (0.75 g/s), transient (1 g/s) and turbulent (1.25 g/s).
Figure 8 Photos of plasma jets impinging onto flat substrate at different regimes of outflow: (a) – turbulent (Re=820); (b) – quasi-laminar (Re=580). (c) – heat flux density from the nitrogen plasma jet to the flat substrate vs. mass flow rate of nitrogen and Reynolds number. curve 1 – $\zeta=6$, curve 2 – $\zeta=8$, curve 3 – $\zeta=10$, $\zeta = z/d$ is non-dimensional distance from the plasma torch nozzle to obstacle.

Figure 9 Cross cut of Ni-Cr-B-Si-C coating sprayed in turbulent regime of plasma jet outflow – (a), and fused by quasi-laminar plasma jet – (b).

5. Applications of cascade torches for powders processing
In the present-day industry of structural and protective materials, powders made up by hollow spheres, or hollow powders, gain increasing acceptance. Hollow ceramic powders are used in the production of plasma-sprayed thermal barrier coatings, composite heat- and sound-insulating materials, light construction fillers and backfills, buoyancy materials, and explosive mixtures. Such powders also form basis for catalysts, adsorbents, filter elements, encapsulating media, etc. HOSP powders can be produced by different methods [10].

Great interest has been recently expressed in studying the characteristics of thermal barrier coatings sprayed from HOSP YSZ powders [11-13], etc. Figure 10 shows photographs of the initial (a) and plasma treated (b and c) spray-dried YSZ powders. Particles were injected radially into the plasma torch exit region to undergo spheroidization in quasi-laminar jet. Working gas – air+CH₄, electric power – 75 kW, four-point powder injection, productivity of process - 20 kg/h.

Another example illustrates the synthesis of $\alpha$-Al₂O₃ hollow powders (figure 11) under plasma treatment of aluminum hydroxide particles from 40 to 120 $\mu$m in size, containing from 10 to 15 wt.% of chemically bound water, in air plasma jet flowing out in quasi-laminar mode of 50-kW cascade gun [14].

At the same time, in our publication [14], the experimental data regarding the novel class of corundum powder particles is presented. They have a size of 40-250 $\mu$m, a specific surface area of 150-200 m²/g and characterized by multi-level inner structure (nano-, submicron- and micrometer) produced by plasma treatment of initial aluminum hydroxide powder under transient and turbulent plasma jet outflow. Figure 12 shows the morphology and texture of the obtained powder with particle
sizes from 90 to 120 μm.

As it can be seen, the α-Al₂O₃ powder particles with rounded surface are formed by crystallites from nano- to micrometer in size. In accordance with derivatographic data, the obtained alumina sample, exhibiting a polycrystalline surface, contained 2.25 wt.% of γ-Al₂O₃ and 2.27 wt.% of more high-temperature phases. Thus, the synthesized alumina is 95 wt.% of α-Al₂O₃ (corundum). This fact was also confirmed by x-ray data. This powder and articles sintered herefrom (tablets, hollow cylinders) are of considerable interest as thermostable catalysts supports.

![Figure 10 SEM photos of initial spray-dried YSZ powder - (a), and HOSP powder made using the cascade torch: (b), (c) – particles’ general view and their cross cut, correspondingly.](image)

![Figure 11 SEM photos of the hollow α-Al₂O₃ spheres - (a), and broken single hollow α-Al₂O₃ microsphere illustrating the shell's thickness - (b).](image)

Finally, with the example of SiO₂ powder we have shown the possibility to synthesize the hollow particles several tens of micrometers in size (see figure 13) using the cascade torch treatment of the suspended nano- and submicrosized powder [10]. On injection into the plasma, the liquid suspension was atomized into droplets that contained quartz particles (mean particle size 110 nm). The droplets were several tens of micrometers in size. On droplets evaporation, the plasma conditions led to the formation of agglomerates of the initial SiO₂ particles, whose subsequent heating and melting resulted
in the formation of hollow spheres.

![Figure 12](image1.png)  
*Figure 12* SEM photos of single α-Al₂O₃ particle characterized by multi-level (nano-, submicron- and micrometer) structure - (a), general view of powder - (b).

![Figure 13](image2.png)  
*Figure 13* Suspension powder plasma treatment (a): 1 – pressure vessel filled with suspension, 2 – high-pressure gas pipeline, 3 – injectors, 4 – plasma gun; appearance of the plasma-synthesized HOSP SiO₂ powder (b).

6. Conclusions
Unique dominating platform based on “cascade” approach allows the satisfaction of practically all customer existing and future needs:

1) Cascade family of plasma torches is easy scaled up and possesses an extremely wide operating window, allowing reproducing plasma parameters and related coatings of practically all torches presently available on market place.

2) Cascade design has capability of generating laminar, transient and turbulent plasmas using different plasma gases; it could allow to develop new coatings and powders.

3) Cascade process is capable of using inexpensive gases to generate plasmas; latter should allow expanding business in developing countries where high purity Ar, He, H₂ are expensive and have some availability problems.

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