THERMAL PLASMA and NEW MATERIALS TECHNOLOGY

Volume 2:
Investigations and Design of Thermal Plasma Technologies

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STATE-OF-THE ART OF THERMOPHYSICAL FUNDAMENTALS OF PLASMA SPRAYING

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The state-of-the art of the thermophysical fundamentals of plasma spraying and some allied technologies of powder plasma processing are presented. In this connection, it has been attempted to analyze the theoretical aspects and experimental data characterizing the processes which take place in plasma spraying, and information about the modern means of their modelling and diagnostics. The survey is composed to enable examination of the range of the questions corresponding to the complete chain of phenomena occurring in the 'plasma torch – powder injection into the plasma flow – formation of a dusted plasma jet – impact of individual particles on the substrate – formation of sprayed material – its further thermal treatment' chain. The information presented may be interesting to scientists and engineers studying plasma and other technologies based on the use of high-temperature flows with a disperse phase.

1 Introduction

Plasma spraying is one of the promising methods of producing coatings and composite materials. Because of a wide temperature and dynamic range of plasma jets and the possibility of using various plasma-forming media (neutral, oxidizing, reducing, etc.), it is possible to combine in a single process both phase and chemical transformations, ensuring the required modification of initial powders, and spraying materials with the required structural heterogeneity.[1–8]

Analysis of the possibilities of plasma spraying shows that, in addition to the traditional application of this technology as a method of depositing protective coatings with various properties, plasma spraying technology is also highly promising if it is regarded as a method of continuous joining of materials.

Even greater possibilities exist in parallel or consecutive combinations of plasma spraying with other technologies. If in the former case the final product is obtained during a single technological cycle, combined with spraying, then in the latter case the spraying material is a semi-finished product and requires finishing treatment to produce the target composite material. In fact, the plasma spraying methods may be used to produce all types of composites, including dispersion hardened, laminated, with a filler, directional solidification, etc.

However, plasma spraying is a highly science-intense technology, and the potential of plasma spraying is far from completely utilized because the 'plasma generator — high-temperature processing flow – sprayed material' system has been studied insufficiently. Advances in this area can be made only by formulating detailed investigations which would gradually include all links of the chain of formation of a stable final product with the required properties guaranteed not only under laboratory but also production conditions.

To formulate these investigations, we have proposed the concept of the complex experiment (CE) in thermal spraying of coatings.[4,5,9] Gradual application of this concept makes it possible to improve greatly the reliability of the results of fundamental and applied investigations as a result of a rational combination of the possibilities of physical and computing experiments.

For efficient application of CE, it is essential to make rapid advances in understanding the physical processes forming the base of this and of a number of allied technologies, and it is also necessary to develop and improve methods for their effective investigation and optimization. In this study, we shall analyze the current state of investigations of thermophysical processes with special reference to plasma spraying powder coatings in the normal atmosphere (APS-process).

In this connection, it is necessary to mention that the potential of the APS-process has not been sufficiently examined. At the same time, it is well known that an alternative of this technology is plasma spraying at reduced pressure (LPPS-process). However, the cost of equipment and produced coatings in the latter case is considerably higher than that in the APS-process. A number of other processes of thermal spraying powder coatings have been proposed in the last decade (HVOF, the hybrid spraying method, [3] etc.).

To determine potential 'technological niches' and scientifically justified application of these technologies, including in this list also a number of other traditional processes (detonation spraying, metallization, etc.), it is essential, on the one hand, to understand in greater detail the basic fundamental phenomena and, on the other hand, formulate simulation investigations to obtain additional data on the advantages and disadvantages of various mutually interlinked technological processes.

In the last 20 years, a number of reviews have been published in the area of thermophysics of powder coating spraying.[4–6,10–13] They reflect the state of investigations of problems forming the basis of this extremely important and promising technology. In addition, successes in this technology may predetermine products also in a number of allied technologies (spheroidization and densification of powders, the O'Spray process, microatomization of powders, etc.).

Taking into account the fact that in a single article it is not possible to deal with the entire problem, the aim of this study is, firstly, to present information on the investigations carried out at the Laboratory of Plasma Dynamics of Disperse Systems of the Institute of Thermophysics of the Siberian Division of the Russian Academy of Sciences. Secondly, utilizing this possibility with no large restrictions on the volume of the particle, we shall attempt to deal with the entire chain of thermophysical problems determining the 'plasma generator– formation of the technological flow–coating' system. Finally, we shall attempt to systematize the results obtained by various authors over the last decade.

2 Fundamental thermophysical problems of plasma spraying

Since the coating is a heterogeneous material, the main aim of plasma spraying powder coatings is to produce homogeneous layers with the required structure over the spraying spot. For efficient control of the structure of sprayed materials, it is important to make further progress in solving the following principal problems:[14]

1) Investigation of the physical relationships governing burning of the electric arc with an axial gas flow blown onto the arc, and examination of the possibilities of controlling the arc by attachment to the output electrode/anode in order to construct thermal plasma generators ensuring the required quality of the out-flowing jet– stationary nature and axisymmetric form, and also the reproducibility of the gas dynamic characteristics of the jet during repeated activation of the plasma generator;

2) Development and examination of the possibilities of new methods of injecting powder materials into the plasma flow which enable the degree of concentration of the two-phase jet to be regulated and ensure a high uniformity of the distribution of the particle velocity and temperature in its cross sections for the spraying systems; also, to increase greatly the productivity and efficiency of the technological process, including the increase resulting from the powder flow rate/transport gas flow rate ratio;

3) Examination of the interphase transfer of the momentum, heat and mass in high-temperature heterogeneous jets of a multicomponent gas and, in particular, of jets impinging onto barriers, taking into account the flow collisions in the jet, higher loading of the jet with the powder, its polydisperse nature, prior history of supply of the particles, their complex aggregate state in the flow, and also the stochastic nature of the local distribution of the velocity, temperature and size of particles in the cross sections of the jet, including the spraying spot;

4) Examination of nonstationary conjugate conduction-convection heat exchange and phase transformations in interaction of the heterogeneous flow and single melted particles with the sprayed surface, and also further development of the physical fundamentals of coating enabling their laminated structure and service characteristics (porosity, adhesion, cohesion, thermal conductivity, etc.) to be predicted;

5) Examination of a set of processes (heating, phase and structural transformations in the coating material and the substrate, etc.), accompanying heat treatment of plasma-sprayed materials and coatings by means of highly concentrated energy fluxes (electric arc, plasma jet, electron beam, laser radiation).

It is evident that the specific content of the program of investigations in solving the problems described previously should be determined within the framework of a specific conceptual approach forming the basis of development of equipment and improvement of the technological process. We believe that one of promising approaches have been proposed by us in Ref.9, 14 and 15. This approach is based on three principles:

a) Development, investigation and application of plasma generators with interelectrode inserts (IEE),[16] both with laminar and turbulent jet out-flow ensuring guaranteed distributed ('diffusion') attachment of the arc on the anode. This enables axisymmetric plasma flows to be generated;

b) Improvement of methods of injecting powder materials into the plasma flow by transferring to radial–circumferential introduction of the powder to obtain an axisymmetric radially converging flow of particles directly beyond the zone of anode attachment of the arc;

c) Application of replaceable output attachments, including diffusors with hot walls, enabling the gas dynamic structure of the flow to be affected in order to create suitable conditions for subsequent efficient treatment of the powder and its protection against the detrimental effect of the environment (oxidation, dissociation, gas saturation, etc.).

The purposeful development of this approach is promising for practically all science-intensive high-temperature technologies taking place in the presence of a condensed phase because as a result of axial symmetry in the entire generated gas-disperse processing flow it is possible to optimize this flow on the basis of combined physical, computing and materials science experiments.[4,5,9]

It should be mentioned that all these approaches require optimization of the technology of plasma spraying powder coatings by optimizing equipment and thermal- and gas dynamic conditions of the process. However, another method of optimizing technology, with other conditions being equal, is optimizing by designing new powder materials with specified unique properties and development of equipment and technology which would enable the properties of the initial sprayed material to be retained in the coating (see, for example, Ref.17).

Gradually, we shall examine the state of investigations in a number of the previously mentioned problems and developments aimed at improving the technology of plasma spraying powder coatings which, in our view, are of fundamental interest also for other high-temperature technologies based on the presence of the condensed phase.

3 Spraying plasma torches

The requirements on plasma generators become more stringent with the development of technology of plasma spraying powder coatings and also widening knowledge of fundamental processes, characterizing the members of the 'plasma generation –formation of a dust-laden processing jet–formation of sprayed material' technological flow. Work is also being carried out to improve and, at the same time, make more complicated design of plasma generators which, in addition to conventional requirements, important for gas heaters: (i) long continuous operating life (of the order of 100 hours and longer), (ii) possibility of working with various plasma-forming media, (iii) stability and reproducibility of the parameters of the high-temperature flow in repeated activation of the plasma generator, (iv) the availability of data, including the volt–ampere characteristics and the efficiency of conversion of electric energy to thermal energy, should satisfy additional more stringent requirements which take into account the specific features of interphase exchange of momentum, heat and mass of inertia particles processed in the plasma: (i) ensuring the maximally uniform heating and acceleration of particles in the cross sections of the plasma jet, including the section corresponding to the spraying spot, (ii) the availability of data on the fields of velocities, temperature and composition of components in the high-temperature jet for the recommended working conditions of the plasma generator, (iii) use of nozzles/attachments for controlling the flow structure and reducing the extent of mixing the discharged jet with the surrounding atmosphere; (iv) absence in the spectrum of turbulent pulsations of the speed and temperature of the plasma jet of low-frequency fluctuations of the same order with the frequency $f \approx \overline{w}_p / L$, where $\overline{w}_p$ is the mean particle axial velocity at the spraying distance L, because in conventional types of plasma generator designed for spraying the zones of effective heating and acceleration of the powder material are situated within the range of several gauges from the outlet of the nozzle. The classification of plasma generators for spraying powder coatings and processing powder materials by the method of generating a high-temperature gas flow is shown in Fig.3.1.

In addition, the plasma generators are subdivided into turbulent and laminar, with subsonic and supersonic discharge of jets, and with stationary or pulsed operation. They may also differ in the method of introducing the sprayed powder material into the plasma flow.

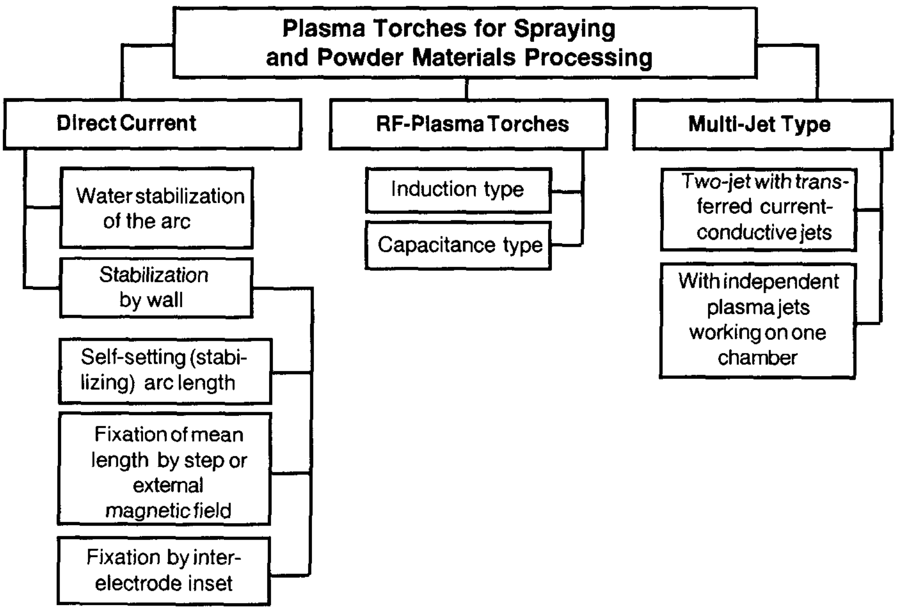


Fig. 3.1. Classification of the plasma devices for spraying and for processing of the disperse materials.

The main type of plasma generator used in powder spraying are direct current plasma torches with stabilization of the arc by the channel wall and, in particular, the simplest type of this plasma generator – plasma generators with the self-setting arc length and with the arc length fixed by a direct or reversed step. These plasma generators are used in standard equipment manufactured by companies Metco, Plasmatechnik, Castolin, SNMI, MTS, Plasmadyne, Miller Thermal Inc., SNECMA, spraying plasma torches used in Poland, etc.

If in plasma generators of medium and high power used for heating gases and stabilizing the electric arc at the axis of the channel it is sufficient to employ extensive twisting of the working gas,[18] then in plasma spraying technology this method of arc stabilization cannot be usually used because of the possible transverse scattering of the powder as a result of the effect of a centrifugal force on the particles. Therefore, the plasma generators for spraying powder coatings usually employ the axial supply of the working gas. When using plasma generators with the self-setting arc length, this results in low-frequency large-scale shunting between the arc column and the channel wall. Disadvantages of this type of plasma generator with special reference to the spraying process have been examined by the authors in Ref.19.

All these factors explain why there is such interest in the problem of improving plasma generators for spraying determined by the importance of using these devices for new technologies and by a number of shortcomings: a) short operating life of the output copper electrode (not exceeding 20 hours in most cases); b) poor reproducibility of the quality of spraying powder coatings; c) problems with using commercial gases, including air.

The first two shortcomings are the result of mainly low mobility of the anode arc spot in the absence of vortex supply of the working gas and also of an unpredictable variation of the area of attachment of the arc in a cylindrical anode both during operation and in the course of repeated activation. Consequently, the fields of velocity and temperatures of the plasma flow in front of the inlet section of the powder material are not constant with time and in space.

The simplest but not always applicable method is to develop suitable conditions for rapid displacement of the support arc spot on the surface of the anode, for example, by affecting the closing part of the arc by aerodynamic or electrodynamic forces. Displacement of the spot, which usually takes place in jumps as a result of shunting, makes it possible to shorten greatly the holding time of the spot in the stationary condition and, at the same time, reduce the mean rate of evaporation of the anode material and increase its service life. In addition, the fields of speed and temperature are averaged out in respect of time and space. The experiments carried out in the past confirm convincingly the positive effect of twisting the anode arc on reducing specific erosion. At a current of 300 A specific erosion decreases almost ten times. As shown by analysis and estimates,[20] the specific erosion can be further reduced by 'diffusion' attachment of the arc spot.

3.1 Main special features of plasma torches with IEI

It is highly promising to use plasma generators with an interelectrode insert (IEI) in spraying powder coatings.

It is well known[20] that the frequency of shunting the arc in plasma generators of this type is one or two orders of magnitude higher in comparison with the shunting frequency in plasma generators with the self-setting arc length, with other conditions being equal. In addition, within a specific range and at the same flow rate of gas, pressure, discharge chamber diameter, arc current and other parameters, the mean mass temperature of the gas at the outlet of the output electrode of a plasma generator with an IEI is always higher than in a plasma generator with the self-setting arc length. This is explained by a higher strength of the electric field of the turbulent arc and by the possibility of varying the length of the IEI. However, if argon is blown into the space between the last section of the IEI and the anode, then, as shown by experiments,[16] the current is uniformly distributed (with equal probability) over a large area of the anode, i.e. there is no attachment of the arc to any area of its surface. Thus, suitable conditions are created for microshunting which may ensure uniform erosion of the internal surface of the anode and also a high uniformity and stationary nature of the distribution of temperature and the velocity of jet discharge of the jet.

For this purpose, it is necessary to fulfil two conditions: (a) maintain the required plasma temperature in the anode region (electron concentration), and (b) reduce the thickness of the boundary layer in the direction along the flow. As the thickness of this layer decreases, the amount of energy lost by the electrons during passage through the cold boundary layer also decreases.

The first requirement is satisfied, in particular, by using low-enthalpy and high thermal conductivity gases, for example, argon.

The second requirement is satisfied by accelerating the flow in the narrowing channel to the speeds equal to the speed of sound. This reduces the thickness of the boundary layer.

An additional factor resulting in equally probable shunting on any point of the separated region of the surface of the anode is the possibility of ensuring a higher frequency of shunting as a result of transition to a developed turbulent arc. As already mentioned, this condition may be satisfied using plasma generators with an IEI.[16] This type of plasma generator was developed at the Institute of Thermophysics of the Russian Academy of Sciences in the last couple of decades and is used extensively in various processes.[18,21] Taking into account these requirements on plasma torches used for spraying, a turbulent plasma torch with an IEI and an outlet copper water-cooled nozzle–anode was developed. A small amount of argon is supplied into the anode zone.[20] The main working gas – nitrogen (a mixture of nitrogen with argon) is supplied into the cathode zone. At 25% supply of argon into the anode zone a transition to distributed ('diffusion') arc attachment takes place. As indicated by Fig.3.2, the specific erosion of the anode material reaches $\overline{G} \cong 5 \cdot 10^{-12}$ kg / C, which ensures not only a long operating life of the anode (more than 100 hours) but also a high reproducibility of the spraying process. As confirmed by experiments, the plasma jet is axially symmetric and the temperature field is quite uniform.

These results show that it is essential to carry out further investigations and expand the theory of 'diffusion' anode attachment of the support arc spot to the surface of the electrode in the zone of the thin boundary layer and, above all, to pay special attention to determining the criteria (conditions) of the stability of diffusion current transfer. It is of further practical interest to examine and develop plasma torches with turbulent and laminar jet discharge ensuring the stable 'diffusion' attachment of the arc on the anode.

3.2 Plasma torch with an IEI and 'diffusion' attachment of the arc on the anode with quasilaminar jet outflow

One of methods of increasing the efficiency and stability of the process of plasma spraying powder coating is to use high-enthalpy flows with a long duration of interaction with the particles of the sprayed material.

In most cases, coatings are deposited using a turbulent plasma flow. The coatings obtained in this manner have usually a density of 90–92% and the bonding strength with the substrate of 1.2–2.0 kg/mm^2. Argon, nitrogen, hydrogen, helium and their mixtures are used as plasma-forming gases. The flow rate of the plasma-forming gas is 40–60 litres/min, and the coefficient of utilization of material (CUM) in spraying over large surfaces is 0.4–0.6. These characteristics of the coatings and the CUM no longer satisfy the requirements of industry. In addition, plasma torches with turbulent jet discharge have the following shortcomings: 1) the plasma flow leaving the nozzle is extensively mixed with the cold surrounding atmosphere and rapidly loses pulse and enthalpy. This reduces the velocity of particles of the sprayed powder, starting at several gauges from the nozzle outlet. The particles cool down and the probability of appearance of incompletely melted particles in the zone of coating formation increases. Oxides and nitrides may also appear; 2) this mixing, together with the dominant effect in the spectrum of turbulent pulsations of the jet leaving the plasma torch with a self-setting arc length with a frequency of the order of 1–10 kHz leads, as shown later, to a large statistical scatter of the values of the particle velocity and temperature (both local and in jet cross sections), reduces the coefficient of utilization of the powder, thus increasing the heterogeneity of the structure of the sprayed coating and reducing its density and bonding strength; 3) turbulent plasma flows are characterized by a high noise level (to 120–130 dB).

One of methods of overcoming problems formed in this case is to generate a long laminar flow at the outlet from the plasma torch (for example, see Ref.22). In addition, plasma generators of this type are promising for processes of treating powder materials where it is also required to generate a long zone of intense thermal or chemical interaction. From the technological viewpoint, it is also interesting to use them in melting sprayed coatings to reduce the general and closed continuous porosity, and increase adhesion.

Figure 3.2 shows the principal diagram and a photograph of a plasma torch developed by us (see Ref.23) which generates jet with a quasilaminar outflow.

The design of the plasma torch is based on a plasma torch with an IEI, small (zero) extension of the cylindrical cathode from the cooled copper collar with a relatively low degree of swirling the working gas introduced into the electric discharge chamber sufficient only for stabilizing the cathode arc spot.

This approach has made it possible to increase the service life of the cathode. Figure 3.4 shows the results of systematic processing a large number of experimental data (working gases were Ar, N_2, H_2) characterizing the specific erosion of tungsten cathodes $\bar{G} = G/(I \cdot t)$, kg/C on the arc current taken from Ref.21. Here G, kg is the mass loss of the cathode during the time t, s at current of I, A. The large scatter of the experimental data (cross-hatched region) is associated with poor thermal contact between the surfaces of pressed-in tungsten and the copper holder. However, if contact is efficient, the specific erosion of tungsten in nitrogen and over a wide range of current is $\bar{G} \approx 10^{-13}$ kg/C. In this connection, it should be mentioned that the degree of erosion of tungsten cathodes with an extension differing from zero used in practice is greater than 10^{-11} kg/C. When working with oxygen-bearing gases, it is recommended to use zirconium cathodes.

In solving the problem of reducing the specific erosion of the copper anode, we have used the following assumptions. The length of the interelectrode insert is selected in such a manner that it is greater than the length of the initial section of the channel at the self-setting arc length. This ensures the formation of a developed turbulent gas flow and a turbulent arc in front of entry into the anode channel. Figure 3.5 shows the dependence of the distribution of current density $\bar{i}$ along a cylindrical anode section of the channel for the given case using argon as a shielding gas. Here $m_a = (\rho u)_a/(\rho u)_o$ is the blowing parameter, the curves 1, 2 and 3 corresponds to the values $m_a = 0; 0.32; 0.67$. The maximum current density is recorded in the initial section.

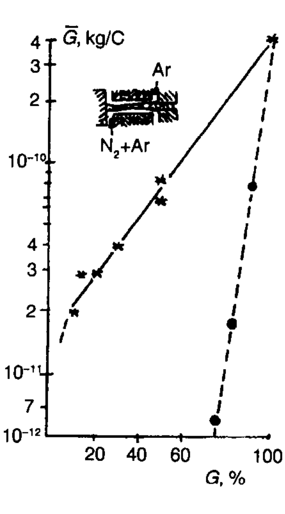


Fig. 3.2

This example shows that when using interelectrode inserts the current is distributed uniformly and with equal probability over a large area of the anode, i.e. there is no 'attachment' of the arc spot to any surface area. In addition, the experiments have shown that the recorded frequency of arc shunting is one or two orders of magnitude higher than the frequency of shunting the arc in the plasma torch with a self-setting arc length, with other conditions being equal.

The calculated and examined plasma torch is designed for operation in the laminar regime. The diameter of its electric arc channel is $d = 12 \cdot 10^{-3}$ m, the length of the IEI is $a = 72 \cdot 10^{-3}$ m; plasma-forming gas is nitrogen (air) with a flow rate of $G = 10^{-3}$ kg/s. The

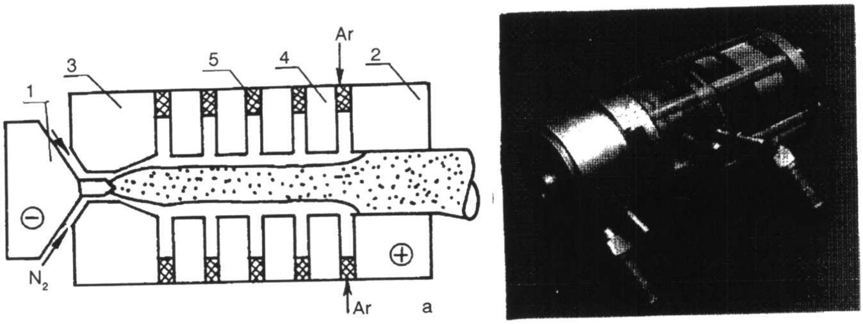


Fig.3.3. The principal diagram and photograph of the plasma torch.

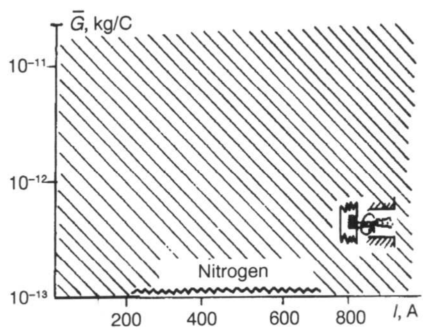
speed of the gas at the outlet from the tangential channels of the swirling ring is 100 m/s. Argon is supplied at a flow rate of $0.2 \cdot 10^{-3}$ kg/s and a circumferential speed component 70 m/s. The plasma torch anode is cylindrical.

Volt–ampere characteristics (VAC) of the arc. Its dependence on the current is shown in Fig.3.6a. In the current variation range 200–300 A and at a nitrogen flow rate from $0.4 \cdot 10^{-3}$ kg/s to $1.2 \cdot 10$ kg/s, they are almost independent of current (hard characteristics), thus ensuring a high electrical efficiency of the plasma torch close to unity.

At the same time, we obtained the dependence of thermal efficiency on current under the same working conditions of the plasma generator, Fig.3.6b.

In the current range 200–300 A and the examined nitrogen flow rate range, the mean mass temperature of plasma is in the range from 6000 to 7000 K.

Effect of the geometry of the outlet part of the anode nozzle on the jet characteristics. We examined three types of outlet electrodes: cylindrical, diffusor (with an angle of 10°), and with a step (Fig.3.7). The best results were obtained with the last type at a ratio of $\Delta l/\Delta r \leq 5$ at which the discharged jet does not interact with the channel wall behind the step.[24, 25] In this case, an additional mass of gas penetrates into the internal region of



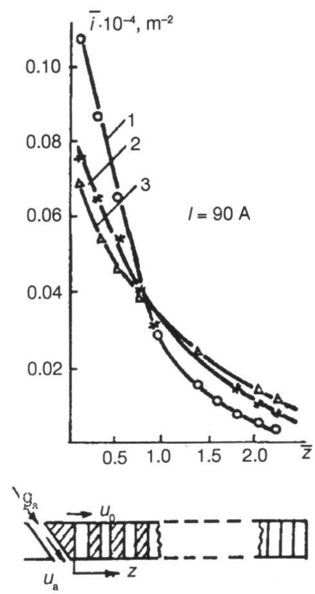


Fig.3.4. The specific erosion of tung-sten cathodes. (left)

Fig.3.5. The dependence of distribu-tion of current density along a cylindrical anode section. (right)

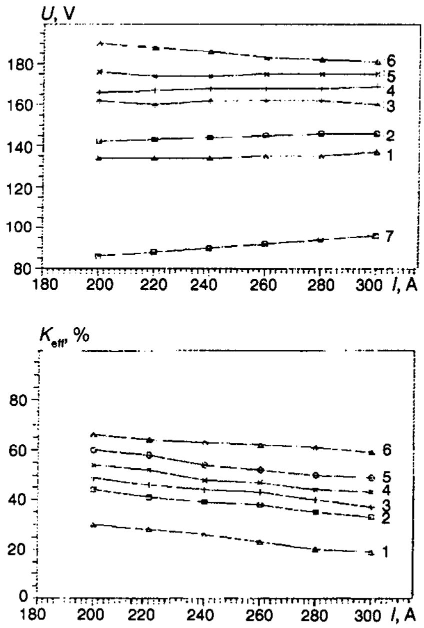


Fig.3.6. Volt–ampere characteristics of the plasma torch (a) and its thermal efficiency. G_{N2}, g/s: 0.4 (1); 0.6 (2); 0.8 (3); 1.0 (4); 1.2 (5); 2.0 (6). G_{Ar}, g/s: 1.0 (7).

the step part from the atmosphere thus ensuring additional stabilization of the discharged jet consisting of reducing the level of turbulence of the flow at its boundaries in discharge into the environment. This is confirmed by the radial distribution of jet temperatures in the sections $\bar{z} = 5$ and 10 for three types of outlet electrodes, Fig.3.7; the graphs show that the most active scattering of jet energy takes place in the diffusor outlet electrode. For the electrode with a step we also obtained the maximum axial temperatures. The cylindrical outlet electrode occupies an intermediate position.

The dependence of the effective power of the plasma torch N (enthalpy flow) on the flow rate of the plasma-forming gas (Re number) at $I = 240$ A is shown in Fig.3.8.

For nitrogen plasma, the transitional value of the Reynolds number (Re = 580) was determined by experiments on the basis of measurements of integral heat fluxes into a flat surface, for different values of distances between the nozzle exit and the surface.

Figure 3.9 shows photographs of jets leaving the nozzle of the plasma torch at Re = 580 and 820 (the distance from the outlet of the nozzle to the barrier was 8 gauges). In the second case, a cooled gas flows onto the barrier and the intensity of this flow increases with increasing Reynolds number.

4 METHODS OF INJECTING POWDER MATERIALS INTO THE PLASMA FLOW

4.1 Comparative qualitative analysis of various injection methods

The productivity and efficiency of the processes of treatment of dispersed materials in plasma jet are determined to a large extent by the method of introducing the powder into the high-temperature flow. At the given thermal power of the plasma generator the efficiency of heating the particles depends on the duration of their stay in the high-temperature zone of the processing flow. The selection of the injection area and the initial velocity of the particles should be matched in such a manner as to ensure

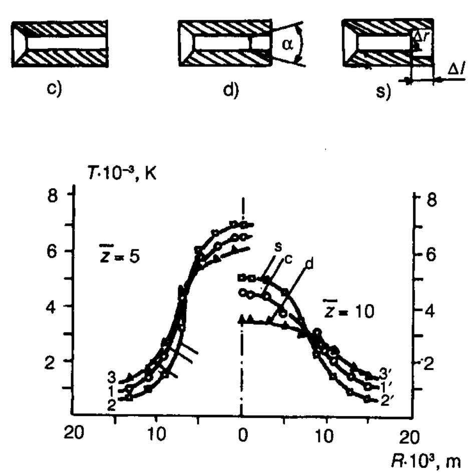


Fig.3.7. Comparison of the temperature profiles for three types of the outlet electrode (c-cylinder, d-diffusor, s-step).