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Effect of Reactive Plasma-Forming Gases on Plasma Spray Operating Conditions: A Technical Note

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Modern plasma spray coating technology allows the use of high-enthalpy plasma-forming reactive gases. Plasma gun thermal efficiency, which defines spray output and coating quality, can be increased. Unlike the argon plasma jet, the CH_4-CO_2 plasma jet oxidation/reduction potential is adjustable and has an enthalpy that is seven to ten times higher. Argon-based gas mixtures are most appropriate for spraying materials that exhibit a high chemical affinity for reactive gases. Otherwise, mixtures of CH_4 and CO_2 are preferable because of higher enthalpy, lower cost, and the possibility of improving the working conditions of the plasma gun electrodes. A universal plasma gun has been developed that uses various plasma-forming gases. The choice of gas depends on the specific plasma spray technology requirements.

1. Introduction

THE plasma torches and plasma spray guns currently used in industry were originally designed in the 1950s (Ref 1, 2). Such torches operate only when low-enthalpy argon or argon-based mixtures containing hydrogen, helium, or nitrogen are used as the plasma-forming gas. The only way to increase the torch power is to increase the arc current up to 500 to 1000 A. However, at such high currents cathode and anode deterioration increases because of high heat flux density (up to 10^8 W/m^2) (Ref 3, 4). Complex and expensive torch designs are required to increase electrode service lives.

Argon and the other gases are used because they are inert with respect to tungsten, the only metal currently used for plasma torch cathodes. In principle, torch performance could be improved by replacing tungsten with another refractory emissive material that can operate in reactive high-enthalpy gases for reasonable lifetimes.

This approach has become possible through the development of new-generation cathodes. A typical application of this approach is air/oxygen plasma arc cutting performed with a torch that incorporates a hafnium or zirconium "thermochemical" cathode (Ref 5-7). Another application is plasma spray coating that employs a plasma gun with a "continuously restoring" cathode and plasma-forming mixtures of hydrocarbons and carbon dioxide (Ref 8-10).

Nomenclature

c	specific heat (J/kg/K)
I	arc current (A)
m	cooling water mass flow rate (kg/s)
P	power, heat losses (kW)
T	temperature (K)
V	arc voltage (V)

Greek symbols

Δ	gradient
η	plasma torch efficiency (%)
Σ	sum total

Subscripts

a	arc
c	calorimeter
eff	effective
el	electrodes
j	plasma jet
th	thermal

2. Cathode Classification

Cathodes for direct-current electric arcs can be classified according to their interactions within the arc gas atmosphere (Table 1).

Table 1 Features of various cathodes

	Cathode type		
Feature	**Pure**	**Thermochemical**	**Continuously restoring**
Arc gas participation in cathode formation	No role	Formation of compounds with an initial metal insert	Sole source of cathode material
Cathode composition and properties during arcing	Invariable or variable	Variable	Invariable
Cathode state	Dense	Dense	Fine granular
Cathode formation	Formed before arcing	Forms during arc run	Forms during arc run
Cathode lifetime	Limited to ~100 h	Limited to several hours	Unlimited (in theory)

Keywords: calorimeter, cathode, efficiency, hydrocarbons, plasma-forming gas, plasma jet characteristics, reactive gases

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2.1 *Pure Cathode*

If the arc gas atmosphere is inert with respect to the cathode material, then no chemical interaction occurs between them. Hence, it can be assumed that the composition and characteristics of the cathode are invariable during arcing. Thermoionic emission always occurs from the surface of the initially installed pure refractory metal, comprising a small amount of activators with a low work function. Therefore, the cathode can be classified as "pure."

In theory, the service life of a pure cathode can be very long since the only mechanism of its deterioration is thermal degradation (Ref 11). However, depletion of cathode additives takes place due to temperatures and their gradients within the cathode; in addition, the polycrystalline structure of the cathode rearranges to a single crystal (Ref 5, 12). As a result, the work function of the cathode material increases, thermoionic cooling of the cathode degrades, and thermal deterioration of the cathode accelerates. The service life of an activated (thoriated) pure tungsten cathode in an argon or argon-based arc gas atmosphere generally ranges from dozens to hundreds of hours, depending on the arc current.

2.2 *Thermochemical Cathode*

If the arc gas atmosphere contains chemically active components with respect to the cathode material, high-temperature chemical reactions are inevitable. In this case, the real emissive surface is not on the surface of the pure metal but on products of the reactions that occur during arcing. This phenomenon has been used to create "thermochemical" cathodes.

Indeed, the elements hafnium, titanium, and zirconium react with oxygen, nitrogen, and carbon to form stable refractory compositions with a comparatively low work function. Hafnium forms the most stable compositions with oxygen and nitrogen during the arc process.

The mechanism of thermochemical cathode deterioration is complex. During arcing, the initially installed cathode separates into layers of different and changeable composition and characteristics. This separation is determined by chemical reactions and diffusion within the cathode body. As a result, erosion of the thermochemical cathode accelerates considerably, primarily because of brittle fracture arising from high thermal stresses (Ref 5).

Usually, the service life of a thermochemical hafnium cathode in oxygen or air arc gas is much shorter compared to that of a pure cathode in an inert gas atmosphere. It generally does not exceed several hours at an arc current range of 50 to 300 A (Ref 7). Despite this shortcoming, thermochemical cathodes have significant industrial application in plasma cutting when air or oxygen is used as the plasma-forming gas.

2.3 *Continuously Restoring Cathode*

Assume that the arc gas atmosphere contains some refractory elements that volatilize at high temperature and exhibit a work function peculiar to conventional cathode materials. The elements are either in pure form or produced from chemical compositions due to their dissociation in the arc. In this case, under certain conditions, these elements can be deposited on the cathode surface during arcing, and thus the arc gas atmosphere can be an unlimited source for the cathode material. Such "continuously restoring" cathodes have been developed for plasma-forming mixtures containing carbon in the form of hydrocarbons (Ref 13, 14).

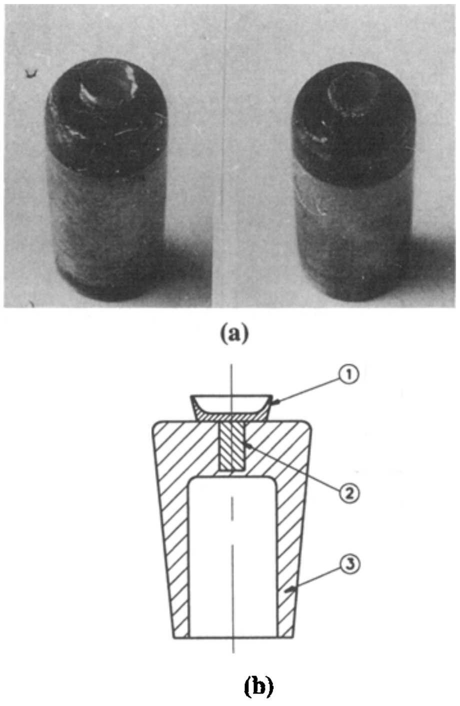

Fig. 1 Continuously restoring graphite cathode. (a) Formed during arcing in a plasma-forming mixture of argon and CH_4 at a current of 250 A. Cathode diameter is 16 mm. (b) Schematic diagram. 1, graphite cathode depositing from a gas phase containing hydrocarbons; 2, cathode insert; 3, water-cooled copper cathode holder

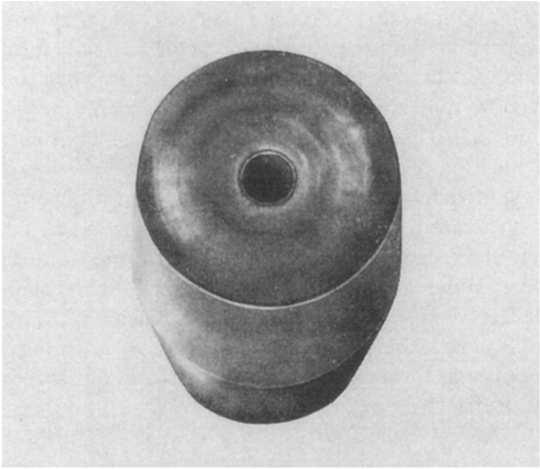

Fig. 2 Continuously restoring graphite cathode formed during arcing in a plasma-forming mixture of CO_2 and CH_4 at a current of 500 A. Cathode diameter is 16 mm

Hydrocarbons dissociate at arc temperatures to form free carbon in both the ionized and neutral forms. Under the influence of an electric field, separation of the plasma-gas-charged particles takes place, and the cathode drop region is enriched by ions with lower ionization potential (Ref 15). The ionization potential of carbon, 11.22 eV, is lower than that of any other element used for forming plasmas. For instance, the ionization potential of helium is 24.5 eV; argon, 15.7 eV; nitrogen, 14.54 eV; hydrogen, 13.5 eV; and oxygen, 13.3 eV. Therefore, in gaseous mixtures containing carbon with any of these elements, the arc current transfer onto the cathode is primarily carried by the carbon ions. Once the carbon ions reach the emissive surface of the cathode and become neutralized, they form a cathode made of fine granular graphite particles (Ref 16). The visual appearance of the cathode depends on the arc atmosphere composition.

If the atmosphere contains a mixture of hydrocarbons and inert gases, particularly argon, the graphite cathode appears as a crown with a wall thickness of about 1 mm (Fig. 1). If the argon is replaced by gases that are reactive with respect to carbon, a surplus of carbon is removed and the shape of the cathode becomes hemispherical, its diameter depending on the arc current (Fig. 2).

When a dynamic equilibrium of carbon loss and carbon formation on the graphite cathode is attained, the cathode is virtually nonconsumable. Its morphology, composition, and characteristics are invariable; that is, the cathode is being continuously restored. Therefore, the wear that is typical for both pure and thermochemical cathodes can be entirely eliminated. In theory, the service life of the continuously restoring cathode is unlimited. It has been proposed that a continuously restoring cathode can be formed during arcing not only for graphite but also for refractory metals that dissociate under arc conditions (Ref 17).

3. Universal Plasma Spray Gun

The universal plasma spray gun is based on the approach discussed in Section 2.3 (Ref 10). The gun is "universal" because it allows use of plasma-forming mixtures of hydrocarbons and carbon dioxide as well as of noble and reactive gases and mixtures. The primary requirement is combination of the plasma-forming gas with an appropriate cathode material; this combination is determined by the plasma spray technology requirements.

Three types of combinations are presented in the sections that follow:

- A plasma-forming mixture of carbon dioxide and hydrocarbons (e.g., methane, or CH_4) with a graphite continuously restoring cathode
- A plasma gas of air or oxygen and a hafnium or zirconium cathode
- A common plasma-forming mixture based on argon gas and a tungsten cathode

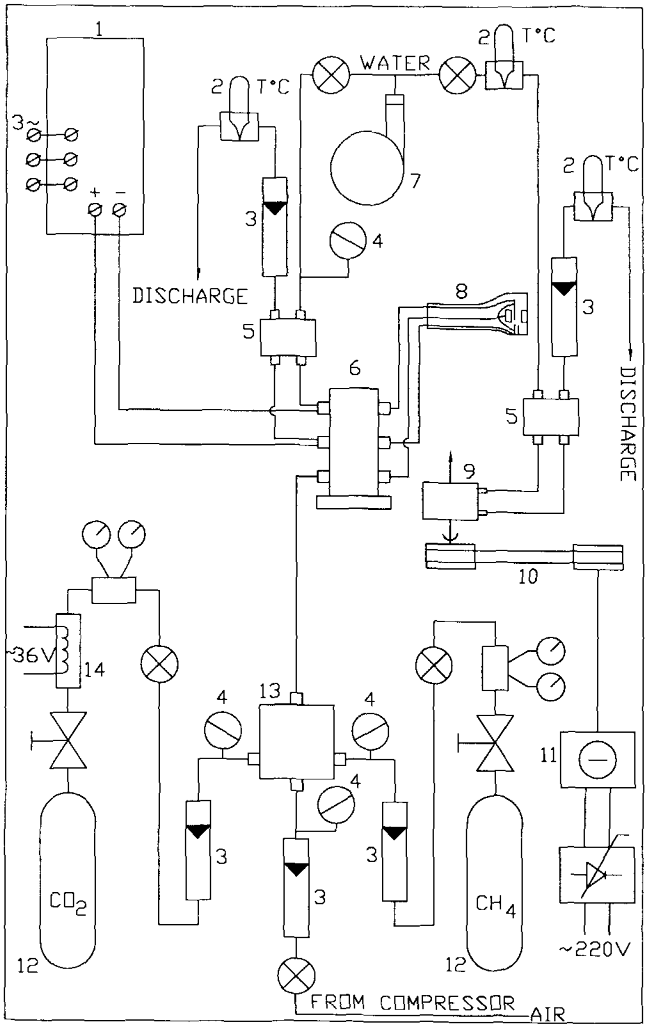

Fig. 3 Schematic diagram of the testing unit. 1, power supply; 2, thermometer; 3, rotameter; 4, manometer; 5, differential thermocouple; 6, electricity/gas/water collector; 7, water compressor; 8, universal plasma spray gun; 9, calorimeter; 10 and 11, calorimeter rotational electric drive; 12, gas cylinders; 13, gas mixer; 14, CO_2 heater

4. Experimental Technique

The effect of gas mixture composition on heat transfer and hence on plasma treatment/heating efficiency was investigated using a plasma jet of reactive gases. The testing unit (Fig. 3) included a water-cooled rotating calorimeter (Fig. 4). A plasma jet was generated using a universal plasma spray gun with three accessory cathodes: a continuously restoring graphite cathode, a hafnium cathode, and a tungsten cathode. A gas vortex was used for arc stabilization.

The arc current variation range of 150 to 300 A corresponded to the real conditions of plasma spraying in high-enthalpy plasma-forming gases and to the permissible current value for the hafnium cathode. The standoff distance from the plasma gun anode to the heated surface of the calorimeter varied from 30 to 150 mm. A range of gas flow rates was determined according to the discussion that follows.

In order to stabilize the arc and ensure longevity of the plasma gun anode throat, the air flow rate must be at least 90 to 100 L/min in the current range of up to 300 A. In addition, CO_2, because of its higher molecular mass, is a better arc stabilizer than air. Therefore, the minimum flow rate of CO_2—in both pure form and when mixed with CH_4—can be reduced to 15 to 25 L/min without any deterioration in plasma gun performance. However, to compare plasma gun efficiency (which depends on the nature of the plasma-forming gas), all experiments were carried out with the CO_2 flow rate the same as the air flow rate.

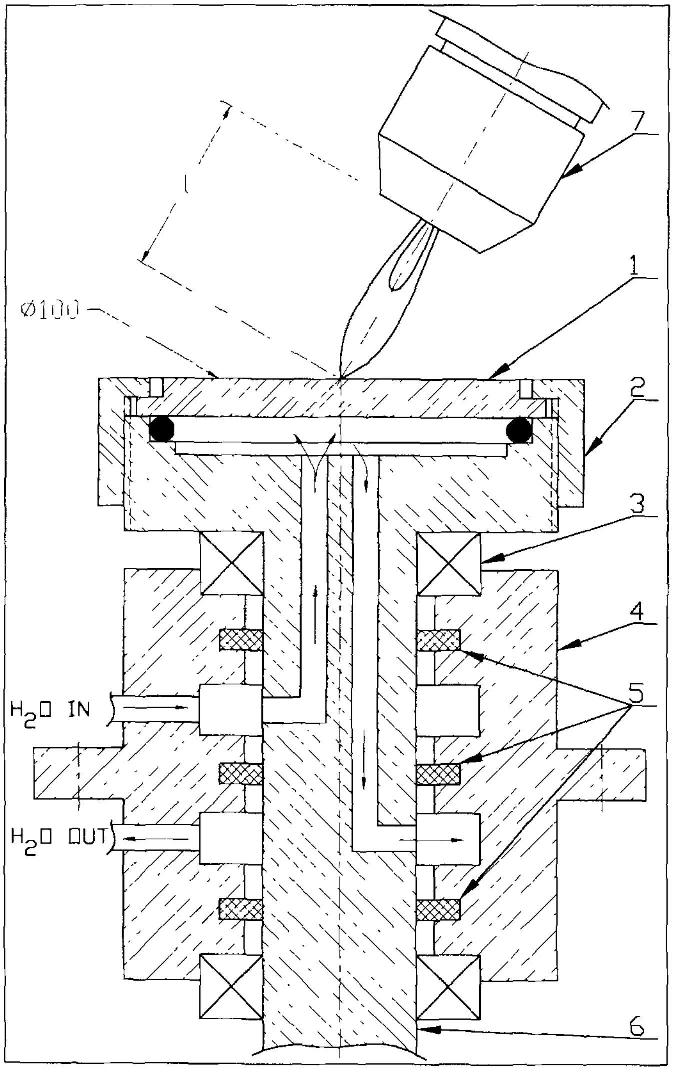

Fig. 4 Schematic diagram of rotating calorimeter. 1, copper disk; 2, nut; 3, bearing; 4, housing; 5, seals; 6, water-cooled shaft; 7, universal

The following parameters were determined in the course of the investigations: arc power, $P_a = V \times I$; total heat losses into the plasma gun electrodes, $\Sigma P_{el} = \Sigma(m_{el} \times \Delta T_{el} \times c)$; and heat release into the plasma jet, $P_j = P_a - \Sigma P_{el}$, and calorimeter, $P_c = m_c \times \Delta T_c \times c$.

These data were used to calculate the thermal (η_{th}) and effective (η_{eff}) efficiency of the plasma torch, thereby characterizing the effectiveness of heating the gas in the plasma torch and of heating the calorimeter (i.e., a plasma-treated substrate):

$$\eta_{th} = P_j \times P_a^{-1}$$

$$\eta_{eff} = P_c \times P_a^{-1}$$

Using thermodynamic analysis based on Ref 18, plasma jet characteristics such as plasma gas composition, enthalpy, temperature, and gas velocity were determined at the exit f the torch anode. The accuracy of the analysis was 10 to 15%. It should be noted that a good coincidence occurred between these results, particularly mean mass gas temperature and gas velocity, and the results of a previously conducted investigation of an argon-based plasma jet (Ref 19).

5. Experimental Results and Discussion

5.1 *Energy Characteristics of the Plasma Jet of Reactive Gases*

Preliminary investigations of the plasma jet in various gases are listed in Table 2. The enthalpy of the plasma jet of mixtures of CH_4 and CO_2 is five to ten times that of the argon plasma jet and is three to four times that of the Ar-H_2 plasma jet. The enthalpy of the air plasma jet is three to four times that of the pure argon jet and about two times that of the Ar-H_2 plasma jet.

Investigations of the heat transfer into the calorimeter from the plasma jet of reactive gases showed that the addition of methane to both CO_2 and air increases the efficiency, η_{eff}, of heating the calorimeter by approximately 6% (Table 3). This is determined primarily by the increase in arc voltage from an increase in electric field strength caused by the presence of free hydrogen in molecular and atomic form.

Indeed, because of the high plasma jet temperature, all the endothermic reactions for the decomposition of methane (CH_4), propane (C_3H_8), and butane (C_4H_{10}) proceed completely, that is:

$$CH_4 \rightarrow C + 2H_2 - 17.9\,\text{kcal}\,(74.45\,\text{kJ})$$

Table 2 Comparative parameters of arc and plasma jet for various plasma-forming gases

Gas	Cathode material	Gas flow rate, L/min	Arc current, A	Arc voltage, V	Arc power, kW	Plasma jet heat release, kW	Thermal efficiency, %	Gas enthalpy, J/kg	Gas temperature, K	Gas velocity, m/s
Argon	Tungsten	30.5	242	50	12.1	6.4	52.9	7.0×10^6	10,500	650
Ar-H_2	Tungsten	50.0	250	80	20.0	12.6	63.0	13.5×10^6	9,050	1100
CH_4-CO_2	Graphite	21.8	230	149	34.3	26.5	77.2	48×10^6	7,500	1220
Air	Hafnium	33.0	230	120	27.6	18.9	68.3	26×10^6	7,000	750

Table 3 Plasma gun energy characteristics when using reactive plasma-forming gases

Gas flow rate, L/min			Arc characteristics			Plasma jet	Plasma gun thermal	Plasma jet characteristics			Heat flow into	Effective
CO_2	Air	CH_4	Current, A	Voltage, V	Power, kW	heat release, kW	efficiency (η_{th}), %	Enthalpy, J/kg × 10^{-6}	Temperature, K	Velocity, m/s	calorimeter, kW	efficiency (η_{eff}), %
77	...	...	230	190	43.7	36.0	82.3	14.4	6700	710	7.3	16.7
72	...	11	230	220	50.6	42.9	84.7	16.7	6200	870	11.3	22.3
68	...	...	300	190	57.0	45.5	79.8	20.4	7100	735	10.0	17.5
65	...	10 3	300	215	64.5	53.0	82.2	22.6	7000	950	14.8	23.0
...	92	...	230	200	46.0	35.8	77.7	18.1	6500	610	5.1	11.1
...	88	10.8	230	235	51.8	39.3	75.9	19.3	5900	660	9.2	17.8
...	110	...	300	205	60.2	44.6	74.1	18.8	6500	600	7.8	13.0
...	98	11.8	300	235	70.5	51.9	73.6	22.9	6200	850	11.7	16.6

Table 4 Comparative characteristics of various plasma-forming gases and gaseous mixtures used for plasma spraying

Gas or gaseous mixture	Arc voltage	Plasma jet properties: Enthalpy	Temperature	Velocity	Thermal efficiency	Electrode wear	Cost	Possibility to adjust oxidizing/reducing gas atmosphere	Noise
Argon	Lowest	Lowest	High	Medium	Lowest	Low	High	No	Lowest
Ar-He	Medium	High	Highest	High	Medium	Medium	Highest	No	Low
$Ar-H_2$	Medium	High	Medium	High	Medium	Medium	High	No	Medium
Nitrogen	High	Medium	Lowest	Low	High	Medium	Low	No	High
Air	High	Medium	Medium	Medium	Medium	Highest	Lowest	No	High
CH_4-CO_2	Highest	Highest	High	High	Highest	Lowest	Low	Yes	High

$$C_3H_8 \rightarrow 3C + 4H_2 - 25.1\ \text{kcal}\ (104.67\ \text{kJ})$$

$$C_4H_{10} \rightarrow 4C + 5H_2 - 30.2\ \text{kcal}\ (125.66\ \text{kJ})$$

Improvement of the heat transfer from the plasma jet also takes place due to the exothermic conversion of CO into CO_2 (Ref 20).

With other conditions constant, the minimum value of η_{eff} (7.8%) is recorded when only air is used. The value of η_{eff} increases to 17.5% when CO_2 is used and reaches a maximum of 23% for mixtures of CO_2 and CH_4.

The higher molecular mass of CO_2 in comparison with air (29 versus 44) results in less spreading of the CO_2-based plasma jet and a lower degree of energy dissipation into the surrounding space. From this viewpoint, the CO_2-CH_4 mixture is identical to Ar-H_2 mixtures. In both cases, hydrogen determines the plasma torch energy characteristics. The arc stability and the gas dynamic characteristics of the plasma jet are determined by the heavy molecular or atomic gas constituents, which are approximately equal (44 for CO_2, 40 for argon). An additional advantage of CO_2 is that it has a much higher enthalpy than argon.

5.2 *Use of Reactive Plasma-Forming Gases in Plasma Spraying*

The experimental results confirm the essential benefit of high-enthalpy reactive plasma-forming gas mixtures enriched by hydrocarbons, in particular CO_2-CH_4 mixtures, with respect to energy balance. A critical question, however, is whether coating quality can be maintained using these mixtures instead of plasma-forming noble gases and mixtures based on them.

The conventionally used argon-based atmospheric plasma spray jet, by its very nature, contains the reactive gases of a surrounding atmosphere. A number of researchers (Ref 21-23) have demonstrated the existence of a pumping effect in the arc jet. This effect cools down the plasma jet very quickly when the jet flows in an ambient gas atmosphere. The effect increases with increasing arc current. Mixing the plasma jet with the surrounding gas atmosphere, usually air, which is pumped very rapidly, inevitably involves variation of the plasma gas composition. The most important effects are the dissociation of both the oxygen molecule above 3500 K and the nitrogen molecule at approximately 7000 K. As a result, the gas composition represents (for example) only 30 vol% of the initial composition 30 mm downstream from the nozzle exit (Ref 22).

In addition, the plasma jet gas velocity is high and thus the speed of sprayed particles is rapid. Therefore, the time of the particle surface contact with reactive gases in the plasma jet, for most feedstocks, is usually much less than that necessary for the completion of chemical reactions defined by their kinetics. Furthermore, by varying the initial component concentration of the CH_4 and CO_2 mixture, the plasma-jet gas atmosphere can be adjusted from oxygen rich to hydrogen rich to neutral. For example, at the conditions indicated in Tables 2 and 3, the gas atmosphere of the plasma jet at the anode exit can be enriched by atomic oxygen in an amount ranging from 0.07 to 0.42 mol. The amount depends on the initial plasma-forming gaseous mixture flow rate as well as on the CO_2 to CH_4 ratio and the arc current.

The importance of free oxygen in the plasma jet was emphasized by G.M. Herterick (Ref 24). In particular, it was found that an oxygen-rich atmosphere of the plasma jet results in improved density and higher hardness of metal oxide coatings.

Finally, it should be mentioned that combustion flame spraying using only reactive gas mixtures of hydrocarbons (acetylene, propylene, propane, etc.) and an oxidizer (oxygen, air) is the oldest of the thermal spray coating methods and has found numerous applications. Reactive gas mixtures of acetylene and oxygen are also used during high-velocity oxyfuel spraying.

5.3 *Comparative Analysis of Various Plasma-Forming Gases*

A comparative analysis of the plasma spray process has been conducted based on Ref 24. Table 4 outlines the properties considered and the advantages and disadvantages of various conventionally applied plasma-forming gases and their mixtures, as well as of the proposed gas mixture of hydrocarbons and carbon dioxide.

Mixtures of CO_2 and hydrocarbons are nonflammable (Ref 25, 26). Another advantage of the CH_4-CO_2 plasma jet is the manufacture of zirconia, alumina, and other refractory ceramic coatings covering large surface areas (Ref 27).

Plasma-forming mixtures of CO_2 and hydrocarbons have been applied successfully in a number of industries in the former USSR to produce a variety of high-quality ceramic, metal, cermet, intermetallic, metal/polymer, and metal/graphite composite coatings used as thermal multilayer barriers, slag resistance overlays for furnace linings, wear/corrosion-resistant coatings, galling-resistant coatings for rolling-contact bearings, low-friction overlays for unlubricated bearings, electrical conductive/insulating coatings for both steel and aluminum electric current leads, and for reconditioning worn parts (Ref 9).

6. Conclusions

The use of plasma-forming gas mixtures of CO_2 and hydrocarbons creates unique opportunities for increasing spray efficiency, improving coating quality, extending the service life of plasma spray gun electrodes, varying the chemical composition of the plasma jet through a wide range, and improving the cost effectiveness of thermal spray coating manufacture.

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