Benefits of Hydrogen in a Segmented-Anode Plasma Torch in Suspension Plasma Spraying

Alice Dolmaire¹ · Enni Hartikainen¹ · Simon Goutier¹ · Emilie Béchade¹ · Michel Vardelle¹ · Pierre-Marie Geffroy¹ · Aurélien Joulia²

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Abstract Suspension plasma spraying (SPS) enables the production of various coating microstructures with unique mechanical and thermal properties. Aeronautical manufacturers have been working for fifty years to improve the thermal barrier coating (TBC) performances in gas turbines. Commercial plasma torches with a segmented anode that are characterized by stable plasma jets should enable a better control of the TBC microstructure. The addition of diatomic gases such as hydrogen in the plasma-forming gas affects the plasma jet formation and causes some instabilities. However, it enhances the thermal conductivity of the gas flow, the plasma mass enthalpy and the heat transfer to particles. This study aims to characterise and describe the coating microstructure changes of yttria-stabilised zirconia when gradually adding hydrogen with argon into the plasma gas mixture. The effect of hydrogen is weighted out due to the gas mass enthalpy, mean velocity at the nozzle exit and “hot zone” length of the plasma jet. The coating microstructures, which depend on these plasma jet parameters, will be mapped from feathery and porous to dense and cracked deposits depending on the spraying conditions.

Keywords columnar coatings · hydrogen · microstructures · plasma jet enthalpy · suspension plasma spraying · thermal barrier coating · Yttria-stabilised zirconia

Introduction

Hydrogen is the most used diatomic gas in spraying plasma torches. It is frequently introduced as a secondary gas to enhance the net power of the torch and increase the temperature of the thermal treated material. Several papers in the literature set out their issues on the effect of hydrogen on “in flight” particle parameters (velocity, temperature, enthalpy) and consequently on the deposit characteristics (Ref 1–5). H₂ was studied more particularly in the context of optimization of coating microstructures in air plasma spraying (APS) using “in flight” measurements such as fast pyrometers and imaging or “time of flight” velocimetry (Ref 6, 7). The percentage of hydrogen in the plasma gas has been considered one of the most important parameters mastering plasma torches; the other important parameters being the arc current and primary gas flow rate. It is often used with argon but also with nitrogen (Ref 2, 8). Bisson et al. (Ref 9) studied the effect of hydrogen on the microstructure of TBC coatings elaborated by APS. Better deposition efficiencies (up to 75%) and denser coatings were obtained by increasing the hydrogen flow rate. Most particles (size distribution < 40 µm) are better melted using hydrogen and more easily flatten to form a homogenous deposit with a porosity below 8%. The effects of hydrogen on the standard torch working conditions are well known, i.e. increases in arc voltage (with a factor of two or three), arc voltage fluctuations and torch thermal efficiency (more than 10%) (Ref 9–11). Indeed, the arc attachment in the anode nozzle depends on the thickness of the cold boundary layer. Few percentages of H₂ are sufficient to increase the thickness of this cold zone, constrict the arc in the centre and force its attachment to move towards the nozzle exit (Ref 10, 11). After a downstream movement, an upstream restrike occurs between the arc and

✉ Alice Dolmaire
alice.dolmaire@unilim.fr

¹ University of Limoges, CNRS, IRCER, UMR 7315,
87000 Limoges, France

² Safran Tech, Rue des Jeunes Bois,
78772 Magny Les Hameaux, France

the anode. The resulting voltage fluctuations are oscillating by approximately 30–70% of the mean voltage. The mean arc elongation induces an increase in voltage and global electric power, while lightly decreasing the thermal efficiency.

Recently, Mauer et al. (Ref 12) presented a paper on the role of hydrogen on the torch behaviour in low-pressure plasma spraying (LPPS). They have shown that a small percentage of hydrogen considerably changes the plasma characteristics such as electron densities, species temperatures... In air plasma spraying, phenomena are perhaps less complex because the local thermal equilibrium (LTE) is generally receivable in the jet centre at the nozzle exit, which involves the identical temperature of electrons and heavy particles ($T_{\text{heavy}} = T_e$). Moving away from the jet axis, the number of collisions decreases, and the temperatures of various species become different. Radially, the temperature gradients are consequently higher. Therefore, deviations from LTE may be expected in the fringes. In this zone, which approximately corresponds to $T_{\text{heavy}} < 6000$ K, the thermal conductivity is relatively high due to the H_2 molecule dissociation (Ref 13).

Conventional torches including a single concentric cathode and a monobloc anode have disadvantages in enabling a possibly large voltage shifting over time, high plasma fluctuations and a relatively low deposition efficiency for a fixed parameter set. The newer cascaded plasma torches, with a segmented nozzle and an anode at the end of nozzle, have the advantages of a better stability and a wide operating window (Ref 14, 15). The anode attachment area is fixed, and the fluctuations are limited. Seshadri et al. (Ref 14) compared conventional and cascaded torches and noted large differences of particle thermal and kinetic treatments. The stability is increased, and number of eddies in the periphery is widely attenuated with the cascaded torch. The saturation feed rate for zirconia powders with a wide particle size range ($-45 \mu\text{m} + 145 \mu\text{m}$) is 80 gpm compared to 60 gpm for a conventional F4 torch (Oerlikon, Kelsterbach, Germany). Although they are more complex and expensive, these cascaded torches are the basic tools for the future in plasma spraying (Ref 15).

The injection of very small particles (less than $1 \mu\text{m}$) using a liquid feeding system has been involved in thermal spray for twenty years to obtain nano-structured coatings (Ref 16–18). The large fraction of interfaces is intended to provide higher hardness (small size grains), higher toughness (crack arresting effect), better wear resistance and a low thermal conductivity (Ref 18–24). The interest of the aeronautic industry is mainly growing for TBC (Thermal barrier Coatings) and EBC (Environmental Barrier Coatings). The advantage of this technic called SPS (Suspensions Plasma Spraying) is to be able to elaborate very thin

layers with various microstructures: columnar, dense, homogeneous, feathery... (Ref 25–31). This microstructure depends on many parameters such as suspension load, suspension feed rate or substrate roughness (Ref 25–28, 30). Seshadri et al. (Ref 26) also recently showed that characteristics of the plasma flow, i.e., total gas flow rate and torch net power could affect coating microstructures in SPS. These characteristics can be comprehended physically as changes in fluctuations, mean mass enthalpy, mean velocity, density, viscosity or thermal conductivity of the plasma at the nozzle exit. Meanwhile studies on the treatment of suspension jet injected in a plasma generated from a conventional plasma torch (Ref 32, 33) have shown that plasma fluctuations have a strong effect on the droplet trajectories and heterogeneity of the droplet treatment.

Fewer arc fluctuations greatly increase the homogeneity of the droplet thermal state, and hydrogen greatly changes the plasma properties as observed. This work aims to study the effect of hydrogen on SPS coating microstructures in a cascaded torch. However, we will first present the role of hydrogen in this cascaded torch on characteristics of the plasma jet: arc voltage, arc fluctuations, mass enthalpy, plasma velocity and jet length.

Experimental Methods

In this study, several technics or methods were implemented to elaborate SPS coatings of yttria-stabilised zirconia (8 mol.% Y_2O_3 , IMERYS fused minerals, Laufenburg, Germany) and characterise the plasma jet mass enthalpy, mean velocity, plasma “hot zone” length and arc fluctuations.

The spraying system (Fig. 1) comprises a cascaded torch (TriplexPro-210, Oerlikon, Kelsterbach, Germany), a rotating substrate holder, a pyrometer synchronised to the presence of a moving substrate and several air jets equipped of a closed loop control. The substrates are home-made alumina button pieces (25 mm in diameter; 1 mm in

Fig. 1 Experimental set-up

thickness). Their average roughness is $R_a = 3.5 \mu\text{m}$ and the average maximum peak to valley height is $R_z = 21.6 \mu\text{m}$. The torch and spraying parameters are presented in Table 1. In particular, injection pressure was optimized to each plasma condition (variations in the gas mixture, the total gas flow rate and arc current) using particle image velocimetry (Fig. 2) to ensure that the maximum of suspension droplets is able to penetrate the plasma and is melted from the centre of the plasma jet during spraying.

For this study, each torch parameter set will be denoted using a naming system of four numbers: the first, second, third and fourth numbers indicate the argon flow rate (slpm), helium flow rate (slpm), hydrogen flow rate (slpm) and arc current (A), as follows:

argon–helium–hydrogen–arc current

For example, a spraying condition using a gas mixture of 40 slpm of argon and 6 slpm of hydrogen, which operates at 480 A, will be noted in the following diagrams as 40-0-6-480.

Plasma Enthalpy and Velocity

The mean mass enthalpy of the plasma (H) is classically calculated from electrical parameters (arc current I and arc voltage U), torch efficiency (η) and mass flow rate ($\dot{m}$) (Ref 34) as $H = U * I * \eta / \dot{m}$.

The mean velocity of the plasma (V) is roughly estimated (Ref 34, 35) from the plasma net power (P_{net}), gas isentropic ratio ($\gamma = C_p/C_v$), nozzle section area (A) and working environmental pressure (p_e) such as $V = P_{\text{net}} * \frac{(\gamma-1)}{\gamma * A * p_e}$, assuming a compressible and adiabatic flow in the nozzle. γ evolves with plasma temperature (Ref 36) and decreases from 1.6 at ambient to 1.15 at approximately 13,000 K for a pure argon plasma. The γ mean value was fixed at 1.25, which is consistent with in-house velocity measurements.

Plasma Jet Fluctuations and Measurement

Plasma jet fluctuations are strongly correlated to arc voltage fluctuations. This parameter is easily measured by

directly connecting wires on the torch electrodes with caution. The electrical signal is digitised at 1.7 MHz and treated to estimate the mean voltage $\bar{U}$, voltage standard deviation σ_U , voltage fluctuations $2 \sigma_U / \bar{U}$ (%) and main frequencies obtained by Fourier transform.

Plasma “Hot Zone” Length (or Localisation of Alumina Rod Melting in the Plasma Jet)

Typically, the plasma core is demarcated by isotherms 7000–8000 K, which are very difficult to detect by any means except emission spectroscopy. However, the useful volume of the heat source, which is defined as being the zone where solid particles can heat up, is larger and can extend until the approximate isotherm 3500 K. This value approximately matches with the temperature of a plasma flow impinging an alumina surface at its melting temperature (2326 K) with an overall heat transfer coefficient of $2000 \text{ W m}^{-2} \text{ K}^{-1}$ and a heat rate of 2 MW m^{-2} (Ref 37). The localisation of the melting tip of an alumina rod on the plasma axis enables us to estimate the “hot zone” length available for treating particles. The technique consists in slowly moving the plasma torch towards the alumina rod and noting the position when the alumina surface begins to melt. With an acceptable measuring accuracy of approximately $\pm 1 \text{ mm}$, it is recognised that this parameter is major.

Plasma Jet Characterisation

Before elaborating and analysing the coatings for various parameter sets, it is fundamental to well comprehend the effects of hydrogen additions in a neutral gas plasma (Ar, He). Except for viscosity, all plasma gas properties increase with H_2 addition. At 13,000 K, 10 slpm of H_2 in a 60-slp Ar plasma induces an enthalpy increase from 17.4 MJ kg^{-1} (set: 60-0-0-480) to 21.7 MJ kg^{-1} (set: 60-0-10-480, see Fig. 5). Thermal conductivity K (Fig. 3) increases by only $0.7 \text{ W m}^{-1} \text{ K}^{-1}$ at 13,000 K between these two sets. At approximately 4000 K, the Ar- H_2 mixing presents an important peak of thermal conductivity (corresponding to the H_2 dissociation), which reaches the same

Table 1 Experimental parameters

SPS Spraying parameters		Torch parameters	
Stand-off distance	60 mm	Nozzle diameter	9 mm
Coating surface temperature	500 °C	Arc current	200–500 A
Zirconia mean suspension size (d50 _v)	0.7 μm	Argon flow rate	40–100 slpm
Solvent	Ethanol	Hydrogen flow rate	0–10 slpm
Suspension load	20 wt. %	Helium flow rate	0–20 slpm
Injection pressure	0.3–1.2 MPa

Fig. 2 Picture of suspension injection in the plasma obtained with particle image velocimetry

Fig. 3 Thermal conductivity of an argon plasma, argon + helium plasma and argon + 14% hydrogen plasma (Ref 36). Parameter sets denoted by four numbers: Ar-He-H₂-Current (flow rate in slpm, current in A)

value as at 13,000 K ($2.2 \text{ W m}^{-1} \text{ K}^{-1}$). This peak of conductivity strongly affects the heat transfer to the nozzle walls and induces an increase in arc voltage (much higher for an F4 standard torch than for a segmented anode torch).

Arc Voltage and Fluctuations

Figure 4 presents a recording of the arc voltage (Triplex-Pro) for a plasma composed only of 60 slpm argon (set 60-0-0-480) and a plasma with argon and 10 slpm of

Fig. 4 Voltage recording (TriplexPro) for the argon plasma and the argon + 14% hydrogen plasma. Parameter sets denoted by four numbers: Ar-He-H₂-Current (flow rate in slpm, current in A)

hydrogen (set: 60-0-10-480). The argon arc plasma (set 60-0-0-480) without helium and hydrogen has a mean voltage of $\bar{U} = 95$ V and a standard deviation of $\sigma_U = 2.5$ V. An addition of 10 slpm of H₂ (set: 60-0-10-480) causes a voltage of 120 V and a standard deviation of $\sigma_U = 6$ V. Voltage fluctuations (Fig. 6) of $2\sigma_U/\bar{U}$ increase from 5 to 10%. In comparison with, a mono cathode and non-segmented anode (F4) and for identical plasmas sets (60-0-0-480 and 60-0-10-480), the arc voltage increases from 30 to 52 V, and the voltage fluctuations are from 6 to 60%. With this type of torch (F4), the absolute freedom of movements of the arc in the presence of H₂ includes large fluctuations of voltage and subsequently high variations of the plasma volume, mainly in the flow direction. These pulsations have detrimental effects on the microstructure and quality of coatings. For a cascaded arc torch, voltage fluctuations are reduced, and the arc attachment point moves along the last stage of the segmented nozzle. At the nozzle exit, the arc can always be deformed, which increases the voltage values, but fluctuations are reduced. The measurements in Fig. 5 and 6 appear to confirm this hypothesis. Voltage uniformly increases with H₂ flow rate until 125 V (Fig. 5), while fluctuations percentage presents a maximum (11%) at 2 slpm (Fig. 6), corresponding to a stabilisation of standard deviation and an increasing of mean voltage.

Similarly, the increase in argon flow rate (from 60 to 100 slpm) results in an increase in voltage (from 95 to 110 V) due to a higher drag force on the arc. The voltage fluctuations also increase due to the arc stretching.

Moreover, when the current is increasing, the arc voltage is increasing (unlike in a F4 standard torch) due to the

increase in plasma temperature, while arc fluctuations decrease due to a decrease in anode attachment zone. The increase in arc current, hydrogen and helium flow rate, are combined with an increase in mass enthalpy. In contrast, an increase in argon mass flow rate cannot balance the progression of net power despite a higher thermal efficiency and decreases the mass enthalpy (Fig. 5 and 8).

For a cascaded arc torch, the main frequency peak of the fluctuations (given by Fourier transform) is at approximately 60,000 Hz, and another very weak peak can be noticed at approximately 2500 Hz independently of the gas nature. These frequencies are different from those obtained with a standard torch (F4), which are between 3000 and 6000 Hz and usually correspond to a “restrike mode”. These fast fluctuations (every 20 μ s) of the cascaded torch compared to the particle time of flight (typically approximately 1 ms), are much more effective for performing a uniform heat transfer to the solid or liquid particles than for a standard torch.

Plasma Jet “Hot Zone” Lengths

As mentioned, the length of the plasma jet “hot zone” defined here approximately corresponds to an extended zone where the temperature is above 3500 K. The range of this length greatly varies between 35 and 110 mm (Fig. 7) depending on the set of spraying parameters. Roughly, trends of these “hot zone” lengths versus mass enthalpy are identical to those for voltages versus mass enthalpy, except for argon. Since the argon flow rate is increasing, plasma “hot zone” lengths appear to be stabilising at approximately 75 mm. This increase in flow rate is

Fig. 5 Arc voltage for various parameter sets denoted by 4 numbers: Ar-He-H₂-Current (flow rate in slpm, current in A, accuracy: ± 1 V)

Fig. 6 Arc voltage fluctuations ($2\sigma_U/\bar{U}$) depending on the flow rates (slpm) or current (A)

accompanied by an increase in plasma velocity, which produces a magnified effect of turbulence. Therefore, a lot of air is pumped, and the end of the jet cools down faster. Amongst the secondary gases, the addition of 20 slpm in helium only results in a jet length below 80 mm, whereas hydrogen has an important effect on the “hot zone” length extension. The value of 110 mm is reached by adding 10 slpm of hydrogen due to the increase in enthalpy and thermal conductivity with a high peak at approximately 4000 K, as previously shown.

To complete this analysis of plasma characteristics, the plasma velocities can be calculated. A map of mass enthalpy versus plasma velocity (Fig. 8) is drawn for the standard parameter ranges: the current is 300–500 A, the argon flow rate is 40–100 slpm, the hydrogen flow rate is

0–10 slpm, and the helium flow rate is 0–20 slpm. We note that:

- The arc current is the main parameter that enables an increase in mass enthalpy and mean velocity (see the 60-0-0-300 to 60-0-0-480 sets)
- Inversely, the increase in argon flow rate from 40 to 100 slpm makes the velocity increase by 500 ms⁻¹ and the mass enthalpies decrease by 6 MJ kg⁻¹.
- For a given argon flow rate, an increase in hydrogen flow rate induces an increase in enthalpy and velocity aligned with the evolution of enthalpy and velocity with the arc current (e.g. sets 60-0-0-480 and 60-0-10-480)
- An argon plasma with 20 slpm of helium has approximately identical characteristics (enthalpy-velocity) to an argon plasma with 10 slpm of H₂.

Fig. 7 Hot zone lengths defined at $T(\text{Al}_2\text{O}_3)_{\text{melt}}$ (mm). Parameter sets denoted by four numbers Ar-He- H_2 -Current (flow rate in slpm, current in A, accuracy: ± 1 mm)

- 10 slpm of hydrogen induces up to 5 MJ kg^{-1} more to the mass enthalpy of an argon plasma
- The combination of the three plasma gases (Ar-He- H_2) enables the plasma jet enthalpy to reach values above 26 MJ kg^{-1} .

To conclude, this cascaded arc torch has a very large working range. It is much more stable than a classical torch with a one-piece nozzle, and its fluctuations main frequency is very high. *Hydrogen considerably improves the range of plasma jet mass enthalpy and velocity while*

maintaining a weak level of fluctuations and drastically increasing the plasma jet “hot zone” length.

Coating Microstructures

This subsection aims to answer the following question: *Are plasma jet mass enthalpy and mean velocity sufficient to describe a plasma jet and explain the associated coating microstructure?*

Fig. 8 Plasma enthalpy/velocity mapping, parameter sets denoted by four numbers: Ar-He- H_2 -Current (flow rate in slpm, current in A)

Coating Microstructures of Different Plasma Compositions with Identical Plasma Jet Mass Enthalpy and Velocity Values

Two coatings were sprayed and compared using a couple of parameter sets (60-10-2-480 denoted by A and 60-0-8-480 denoted by B) with approximately identical plasma mass enthalpy (20 MJ kg^{-1}) and velocity (1020 ms^{-1}), but different gas mixture compositions (see mapping of Fig. 17). The first set (A) is comprised of secondary gases of 10 slpm of helium and 2 slpm of hydrogen, while the second set (B) without hydrogen has 8 slpm of hydrogen to compensate the lack of enthalpy and velocity with respect to set A. Coating cross sections are presented in Fig. 9. For comparison, a bar chart graph provides the variation (in percentage) of plasma properties between the two sets, such as plasma mass enthalpy, temperature, velocity, fluctuations, “hot zone” length, column width and micro-metric total porosity of the resulting columnar coatings.

We note:

- A microstructure with rather conical and irregular columns in both coatings.
- Some columns don't seem to start from the interface with the substrate in both coatings.
- An increase in column width (+ 20%) confirms a better densification with the addition of hydrogen.
- Higher porosity (11.5 vol.%) inside columns for set A than set B (8 vol.%).

These microstructures look similar with a better densification for set B (− 30% in porosity). The largest amount of hydrogen for set B (~ 12% of the total gas flow rate, compared to 3% in set A) with a higher thermal conductivity at 4000 K causes an increase in plasma “hot zone”

length (+ 13%) and a longer time of flight in the “hot zone”. A better heat transfer is surely responsible of the changing microstructure.

In conclusion, the plasma jet mass enthalpy and velocity are not sufficient to explain a specific microstructure. The plasma composition (particularly the presence of hydrogen) affects the coating microstructure and compositions.

Evolution of the Coating Microstructure with Increasing Arc Current

This section aims to study the effect of the arc current on the coating microstructure. Plasma properties and coating microstructures of set 60-0-6-300 denoted by C and set 60-0-6-500 denoted by D (see mapping of Fig. 17) are compared below.

The increase in arc current from 300 to 500 A has a beneficial effect on the column compactness (− 8% in porosity) and column width (+ 57%). The column width (Fig. 10) is increasingly broader (from 37 to $68 \mu\text{m}$) with increasing arc currents (from 300 to 500 A). This trend is closely linked to the increase in plasma mass enthalpy and mean velocity (+ 70%), which causes an increase in particle temperatures and velocities, a better flattening on the substrate and a better compactness. It is also combined with a small decrease in fluctuations, and much more interestingly, an increase in “hot zone” length (+ 29%). Therefore, the particle heat treatment is of better quality within the plasma jet. *All evolutions of plasma properties are positive for a better thermal and kinetic treatment of particles.* Furthermore, this increase in plasma jet velocity enables a higher axial component of the particle velocity, which results in a weaker particle divergence. This weak divergence decreases the flux of particles travelling parallel

Fig. 9 Coating cross sections for 2 sets (A and B) with different gas mixture compositions, but identical plasma enthalpy and velocity. Evolution of plasma and coating properties (in %) when set A evolves to set B

Fig. 10 Coating cross sections corresponding to a current increase (from 300 to 500 A). Evolution of the plasma and coating properties (in %) when set C evolves to set D

Table 2 Torch parameter sets (Ar-He-H₂-current) for specific points represented Fig. 16

Point	Torch parameter sets	Point	Torch parameter sets
A	60-10-2-480	G	60-10-0-480
B	60-0-8-480	H	60-10-10-480
C	60-0-6-300	I	80-10-0-480
D	60-0-6-500	J	80-10-10-480
E	40-10-0-480	K	100-0-0-400
F	40-10-10-480	L	100-0-8-400

to the substrate and mitigates the “shadow” effect. Hence, a decrease in column concentration and an increase in their wideness are noted.

To continue this study, four set couples (Table 2) corresponding to an addition of hydrogen (sets E and F, G and H, I and J, and K and L) and the associated coating microstructures were compared.

These four couples correspond to four argon flow rates: 40 (points E and F), 60 (G and H), 80 (I and J), and 100 slpm (K and L).

Does the addition of hydrogen always have a beneficial impact on the coating microstructure? The coating microstructures in connection with associated plasma properties will be closely examined in the following sections to answer this last question.

Effect of the Hydrogen Flow Rate on SPS Coating Microstructures

Coating Microstructures for Sets Including 40 slpm of Ar and 0 or 10 slpm of H₂

The coating cross sections and bar chart graph are presented in Fig. 11 (set 40-10-0-480 denoted by E and set 40-10-10-480 denoted by F). Set F plasma gas has 20% of

hydrogen compared to set E without hydrogen. Such important percentage of H₂ usually greatly changes the plasma properties. From set E to set F, the voltage increases from 94 to 123 V, and the mass enthalpy increases from 22.8 to 27 MJ kg⁻¹.

From set E to set F, the coating porosity decreases with hydrogen increase due to the increase in the “hot zone” length (+ 62%). Columns are broader (+ 20%), and the crack width is smaller due to a better thermal treatment (high increase in hot zone length) and kinetic treatment (+ 19% in velocity). The sharp increase in fluctuations (+ 166%) do not appear to affect the microstructure, due to the very high frequencies (60 kHz) of arc fluctuations. Moreover, as previously mentioned, arc fluctuations for a cascaded arc torch do not affect the heat and kinetic treatment of particles.

The addition of hydrogen boosts the coating compactness at the cost of a small increase in column width.

Coating microstructure for sets with 60 slpm of Ar and 0 or 10 slpm of H₂

The coating cross sections and bar chart graph are presented in Fig. 12 (set 60-10-0-480 denoted by G and set 60-10-10-480 denoted by H). The conditions are identical for the previous couple of sets but with 60 slpm of argon.

- Set G has a more irregular and porous microstructure than for set E with 40 slpm of argon. With respect to set E, the mass enthalpy of set G plasma jet is reduced (from 22.8 to 19 MJ kg⁻¹), and its velocity is increased (from 790 to 970 ms⁻¹). For a roughly similar “hot zone” length (~ 75 mm) and a higher velocity, the time of flight of set G particles and time for heat treatment decrease, so the columns can be more porous.
- The trends between set G and set H are identical to the transition between set E and set F: as a whole, the

Fig. 11 Plasma parameters and coating changes when set E evolves to set F

Fig. 12 Plasma parameters and coating changes when set G evolves to set H

coating microstructure is denser, but some small cracks parallel to the substrate are observed along vertical cracks, particularly in the higher part of the deposit. Due to stress relaxations, these cracks can be linked to the temperature gradient during the process and/or during the cooling of the deposit.

- The column widths for set H and set F are identical (approximately 66 μm), which confirms the identical compactness

The effect of hydrogen addition is the same in an argon plasma with flow rates between 40 and 60 slpm. Specifically, it leads to a lesser porosity and a higher column width.

Because the trends for 80 slpm of argon (sets I and J) are exactly identical, a detailed description of the microstructures is not provided to simplify this presentation.

Coating Microstructure for Sets with 100 slpm of Argon and 0 or 8 slpm of H₂

The last couple of sets (set 100-0-0-400 noted K and set 100-0-8-400 noted L) has identical variations to the previous couples. However, the arc current decreased at 400 A to maintain the plasma jet velocity range at approximately 1000 ms⁻¹. The “hot zone” length for set K is approximately 75 mm for all sets with high flow rates. Indeed, the increase in argon flow rate induces a higher air pumping and jet cooling.

In Fig. 13, the coating microstructure obtained from set K (without hydrogen) is porous with conical columns as expected. The coating microstructure obtained from set L with 8 slpm of hydrogen has narrow and parallel columns (41 μm in width), which is required for TBC.

Globally, the introduction of 8 or 10 slpm of hydrogen in a high flow rate of argon is very efficient to obtain a

Fig. 13 Plasma parameters and coating changes when set K evolves to set L

Fig. 14 Hot zone length defined at $T(\text{Al}_2\text{O}_3)_{\text{melt}}$ for various parameter sets

better compactness and an identical column width. A higher argon flow rate corresponds to more parallel and regular columns.

Synthesis

To obtain a global view of the results, the plasma “hot zone” lengths and coating parameters such as the total porosity and column width are presented in Fig. 14, Fig. 15 and Fig. 16. The plasma gas mixtures of sets E, G, I and K do not contain hydrogen.

The main trends are:

- Hot zone” lengths (Fig. 14) are greatly affected by the presence of H_2 due to the thermal conductivity peak at

4000 K. Without hydrogen in the plasma gas, the “hot zone” lengths are reduced in the range of 70–80 mm. With hydrogen, the plasma “hot zone” lengths are always increasing, up to 130 mm, and the increase is much more effective for small flow rates of argon (+ 62% for set F) than for high flow rates (+ 18% for set L). The H_2 percentage is the most influent parameter on the plasma jet “hot zone” lengths (followed by the arc current).

- The column width (Fig. 15) is globally increasing with plasma mass enthalpy. It is doubled between enthalpies of 12 and 25 MJ kg^{-1} , which correspond to argon flow rates evolving from 100 to 40 slpm. Moreover, the column width increases by 50% with the addition of H_2 and with the increase in arc current. The particle temperature increases with mass enthalpy, while the

Fig. 15 Column width for the studied parameter sets **Fig. 16** Coating porosity for the studied parameter sets

compactness is improved and the crack number is reduced.

- Columnar microstructure evolves a lot with H₂ presence in plasma gas: *total porosity* (Fig. 16) is *decreasing of 30% with addition of 10 slpm of H₂*. Finally, contrary to what one may think, the increase in argon flow rate does not significantly decrease total porosity (see sets F, H, J, L).
- *Mass enthalpy tends to shape the column morphology.* Below 15 MJ kg⁻¹, independently of the plasma jet velocity or percentage of H₂ in the gas mixture, narrow and parallel columns are obtained. Above a threshold in mass enthalpy of 23 MJ kg⁻¹, broad columns of zirconia are obtained independently of the plasma jet velocity. Dense and broad columns are obtained when high-plasma jet mass enthalpies are combined with the highest extension of plasma “hot zone” lengths (more than 100 mm), due to the addition of H₂ at low Ar flow rates (40–60 slpm). The times of flight of particles in “hot zones” are significantly improved in these cases.

The coating cross sections are compiled in Fig. 17. This mapping shows global trends on the effect of the plasma jet mass enthalpy and mean velocity on yttria-stabilised zirconia coating microstructures:

Fig. 17 Coating microstructures in a plasma mass enthalpy-mean velocity mapping

- For a set value of enthalpy, an increase in plasma jet mean velocity causes the compaction and densification of the columns.
- As previously shown, the addition of H_2 in the gas mixture causes broader and denser columns when we compare coatings from plasma jets of identical mass enthalpy and mean velocity.

Conclusions

The main conclusions are:

- With hydrogen, the arc fluctuations ($2 \sigma_U / \bar{U}$) remain below 15%, and the high frequencies of approximately 60 kHz do not affect or barely affect the heat and kinetic treatment.
- The fluctuation increase (up to 15%) with H_2 does not affect the coating microstructures of 8 mol.% yttria-stabilised zirconia.
- The addition of 10 slpm of H_2 in the total gas flow rate on average results in a +15% increase in mass enthalpy and +20% increase in plasma velocity.
- The columnar microstructure greatly evolves with the addition of H_2 in the plasma gas mixture: column compactness and parallelism are greatly improved.
- The column widths mainly depend on the plasma “hot zone” lengths and consequently on the percentage of H_2 in the plasma gas mixture.
- The plasma jet mass enthalpy drives the columnar morphology; below the threshold value of 15 MJ kg^{-1} , narrow and parallel columns are obtained, above the

threshold value of 23 MJ kg^{-1} , broad columns can be attained.

- The plasma jet mean velocity helps in making dense and compact columns for a set value of mass enthalpy.
- An increase in H_2 percentage in the plasma gas mixture causes denser and broader columns of yttria-stabilised zirconia when we compare the coatings obtained with plasma jets that exhibit identical mass enthalpy and mean velocity values.

In conclusion, the benefits of hydrogen in a segmented-anode plasma torch for SPS are straightforward. Its addition to the plasma gas mixture provides a better melting of particles without disadvantages associated with arc fluctuations as in a standard torch and helps to elaborate denser columnar coatings (column width $< 80 \mu\text{m}$).

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