The Research of Yttria Stabilized Zirconia Coatings formed by a low Pressure Thermal Spraying Plasma Torch

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Abstract. To enhance deposit efficiency and improve quality of the coatings of the Yttria stabilized zirconia (YSZ) formed by the thermal plasma spraying method. A new kind plasma touch with diverging-converging nozzle and an internal powder feedstock were designed. The optical emission spectroscopy method was used for evaluating powder molten and vaporized degrees. The results indicated that the plasma jet produced by the two kinds of plasma gases under the 700 a condition made the feedstock powder of YSZ vaporized partially, but different melting degrees. Denser column microstructure YSZ coatings were first successfully deposited at an arc current of 700 A by using Ar-He-H₂ plasma gas. In the Ar-H₂ plasma jet, the temperature is higher at the same axial distance. The micro-hardness of the coatings deposited by Ar-He-H₂ plasma gases is higher.

1. Introduction
The thermal barrier coatings of the YSZ with columnar structure were widely used in gas turbine, which can improve the turbine efficiency. The lamellar and porous microstructure YSZ coatings were used to form the dense electrolyte (Ref 1-3). The above two coatings both can be made by thermal plasma spraying method. The melting and vapour of the feedstock powder in the thermal spraying plasma jet have a great effect on the microstructure of the formation coating.

In this paper, the characteristic of the thermal spraying plasma jet was studied by detect and analyse the optical intensity of the plasma jet. Different microstructure YSZ coatings were deposited by changing the plasma gas and spraying distance. At the same time, a new designed thermal spraying plasma torches was used to form YSZ coatings.

2. Experimental Details

2.1. Plasma nozzle
A plasma spraying equipment for very low pressure condition was developed by the Thermal Spraying Center of the Dalian Maritime University (Ref 4). The pressure in the vacuum chamber could be changed between 100Pa to 10000Pa. Fig.1 shows the schematic sketch of the plasma torch anode.
Inside diameter of the anode is 6mm and a length of 20mm, and the diameter of the single tungsten cathode is 9mm, and the inside diameter of the nozzle is 8mm.

![Figure 1. Schematic sketch of the nozzle and anode](image1)

2.2. Feedstock Materials
In general, the powder particles used in the thermal spray are usually microscopic with the particle diameter ranging from 5 to 100μm. Figure 2 shows the standard ZrO$_2$-7-8%Y$_2$O$_3$ feedstock powder with the size of 80-250nm. The morphologies of the spherical powder with size of 30-70μm after agglomerated and sintered were shown in Figure 2

![Figure 2. Mucilage Adhered Crushed powder](image2)

An Olympus optical microscope was used to observed the cross sectional microstructure of the coating. The OLYCIAm3 software was used to analyse the amount of porosity in the coating. The MH-6 hardness test with a 300g load was used to measure the coating. The Carl Zeiss SUPRA TM55 field emission scanning electron microscope (FESEM) was used to evaluate the cross-sections of the coatings.

2.3. OES Measurement and Thermal spraying process
In the experiments, Optical emission spectroscopy (OES, AvaSpec-2048-4-USB2, multichannel spectroscopy, Avantes, The Netherlands) was used to measure spectrum of the plasma jets. The measurement was performed along the flow axis and perpendicular to the axis of the plasma jet. The
optical fibers connected to the spectrometer transferred the signals of emission spectra. The spectrometer is equipped with a 1200 lines/mm diffraction grating (type Step index Multimode FC4-UV/VIS -200-2-ME). The spectrometer was scanned between 200 and 1100nm by using a 0.2nm step size. A 2048x784 pixel CCD (CCD type SONY2048) collected the signal, and the computer received the CCD signals, which were analysed by Spectra-Lavasoft. The spectral of the spectrometer system should be calibrated before performing the experiments by the Mercury-Argon calibration source (AvaLight-CAL). The experimental equipment for spectroscopic measurements of plasma temperature is schematically shown in Figure 2. The data of the spectrum was analysed by using the PlasusSpecline to identify the atomic lines. And the spectral information of the PlasusSpecline from the US national standard and technology institute were used.

A new kind of plasma torch was used to made coatings under Atmospheric condition. A little hydrogen added into the main gas argon used to improved plasma torch power. The multiply of the voltage between anode and cathode and the current was used to calculate plasma input power.

The plasma torch was used at arc current 700A with two working gases flows of Ar-H₂ mixture (40/10 SLPM Ar/H₂) and Ar-He-H₂ mixture (20/20/10 SLPM Ar/He/H₂). The carbon steels’ substrate with size of 30x30x5mm³ was treated with Sand Blasting before plasma spraying, and then the bond coat was deposited on the substrate by APS. The spraying parameters of the topcoat YSZ coatings were listed in Table 1.

| spraying parameters | Case 1          | Case 2          |
|---------------------|-----------------|-----------------|
| Chamber pressure    | 60 Pa           | 80 Pa           |
| Plasma gases flows  | Ar/H₂ 40/10 SLPM | Ar/He/H₂ 20/20/10 SLPM |
| Ar Carrier gas flows| 5 SLPM          | 5 SLPM          |
| Feed rate           | 10 g/min        | 10 g/min        |
| Spray distance      | 200 mm          | 200 mm          |

The emission line’s absolute intensity is given by:

\[ I_{t,s} = \frac{I}{4\pi} \frac{A_{t,s} n_0}{Z} \exp\left( - \frac{E_s}{k_BT} \right) h\nu \quad (1) \]

Where L is the depth of the emission source, I is the absolute intensity of the emission line of s to t. k is the Boltzmann constant, h is Planck’s constant, n₀ is the total number density of atoms. Eq1 taking the natural logarithm yields:

\[ \ln \frac{I_{t,s}\lambda}{g_s A_{t,s}} = \ln \frac{I h n_0}{4\pi Z} - \frac{E_s}{k_BT} \quad (2) \]

All other terms in Eq5 are constants except for (-Eₛ/kₜₐₜ), and this plot is considered as the Boltzmann plot. Eq5 can be simplified as:

\[ \ln \frac{I\lambda}{gA} = - \frac{5040}{T} E + C_1 \quad (3) \]

Where C₁ is constant, Es would have a linear relationship with a slope of (-5040/T) (Ref 5).
Parameters of ArI species with the wavelength ranging from 675 to 820 nm is listed in Table 2. Electron temperature can be obtained by based on the Boltzmann method.

| λ/nm  | A/s\(^{-1}\) | E\(_\mu\)/eV | g\(_u\) | Ref  |
|-------|--------------|--------------|---------|------|
| 675.284 | 1.93E+06     | 14.74        | 5       | NIST |
| 687.129 | 2.78E+06     | 14.71        | 3       | NIST |
| 714.704 | 6.25E+05     | 13.28        | 3       | NIST |
| 727.293 | 1.83E+06     | 13.33        | 3       | NIST |
| 750.387 | 4.45E+07     | 13.48        | 1       | NIST |
| 772.35  | 11.7E+06     | 13.32        | 3       | NIST |

3. Results and Discussion

3.1. Optical spectrum diagnostic

Figure 3 shows the plasma jet at low pressure with 100Pa with 40Ar-10H\(_2\) and 20Ar-20He-10H\(_2\) SLPM gases without the injected YSZ powder. Compared with the Ar-He-H\(_2\) plasma gas, the plasma jet with Ar-H\(_2\) plasma gases is lighter. So under different gases conditions, the properties of the plasma jet were substantially different.

![Figure 3](image)

**Figure 3.** Plasma plumes at pressure of 100Pa and an arc current of 700A with plasma gases of: (a) 40Ar-10H\(_2\); (b) 20Ar-20He-10H\(_2\).

Figure 4 shows axial distribution of electron temperature of the plasma jet with different gases composition at 700A. At the exit of near nozzle, the temperature of the plasma jets produced by two kinds of plasma gases was almost the same. With the increase of axial detection distance, the temperature of the plasma jet with Ar-H\(_2\) is higher than the one in the Ar-He-H\(_2\) plasma jet at the same axial distance. When the axial distance ranges from 50mm to 100mm, the temperature in the plasma jets with two kinds of gases composition kept constant. And then with the further increase of axial detection distance, the temperature in the plasma jets decreases rapidly. The temperature in the central of the plasma jet was about 5000K at the 200mm axial distance. So the powder in the central of the plasma jets was evaporated, which has a great effect on the microstructure of the coatings.
3.2. *Microstructure and hardness of the coatings*

Figure 5 shows the typical coating microstructures under the spray distances of 200mm. The thickness of the coatings is about 300μm. The coatings made by the Ar-H₂ plasma gases display uniform lamellar microstructure and the micro-hardness of the coatings is about 937HV₀.₃. While the coatings deposited by Ar-He-H₂ plasma gases have much more column microstructure with a lot of small pores, and the micro-hardness of the coatings is about 1186 HV₀.₃. The powder in Ar-H₂ plasma jet can obtain much heat, so fully melted particles and a small amount of evaporated powders helps the formation of lamellar structure. The powders in the Ar-He-H₂ plasma jet can get much higher speed, which made the coatings much denser. The powders of the gas-liquid mixture were deposited onto the substrate. The vapour condensed on the substrate formed the pores.

4. *Conclusion*

It was clearly found that the composition of the plasma gas considerably affect the quality of the coating, due to the different plasma jet characteristic. A new thermal plasma torch under the 100Pa condition was used in this study. The results of emission spectroscope diagnostic showed that the electron temperature in the Ar-H₂ plasma jet is higher than the one in the Ar-He-H₂ plasma jet. The coating microstructure deposited by the Ar-H₂ plasma gases consisted of the lamellar splats from melted particles and the vapour condensation. The coating formed by the Ar-He-H₂ plasma gases display column microstructure, and has the higher micro-hardness.
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