Spray Parameters Influence on Suspension Plasma Sprayed Zirconia coatings properties

Tao Ru
Thermal barrier coatings (TBCs) are a simple and proven method to protect hot section components. Suspension Plasma Spray (SPS), an emerging process technology to generate TBCs, compared with traditional Atmospheric Plasma Spray APS, can deposit thinner coatings with finer microstructure. Operating parameters play an important role in developing certain properties of coating. In this thesis work, power level, gas flow rate, number of spraying strokes, spray gun’s nozzle size i.e. internal diameter and suspension rate were controlled to produce coatings with different microstructures and porosity levels. According to the experimental results, the power level of plasma gun play an essential role on coating microstructure, for instance, the density of vertical cracks increased with growing the power level. The number of spraying strokes showed also an impact on coating porosity. However, due to different nozzle sizes i.e. diameter, the same coating property were controlled by different operating parameters. For coatings deposited by small and large nozzles, their coating thickness and roughness mainly relied on power level and gas flow rate. In contrary, it seems that the coating roughness was not influenced by the same parameters when it was deposited by medium nozzle. Also, gas flow rate do not have as big as influence on coating thickness.
This thesis work has been carried out at the workshop and material labs of University West at the Production Technology Centre in Trollhättan.

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It is my honour to study in University West and work with so many excellent engineers. Thanks you all for giving me so much help in my master study.
Affirmation

This master degree report, *Suspension Plasma Sprayed Zirconia coatings properties*, was written as part of the master degree work needed to obtain a Master of Science with specialization in manufacturing degree at University West. All material in this report, that is not my own, is clearly identified and used in an appropriate and correct way. The main part of the work included in this degree project has not previously been published or used for obtaining another degree.

Tao Ru

Signature by the author

Date

2014. 08. 28

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1 Introduction

1.1 Aim

In this work, axial-injection Suspension Plasma Spraying (SPS) had been used to deposit 8 wt % yttria-stabilized zirconia (YSZ) coatings on stainless steel substrates to investigate the effect of SPS processing conditions on the coating properties including thickness, roughness, porosity and its microstructure. The SPS spray parameters of interest were gas flow rate, power level, number of spray strokes, suspension flow rate as well as nozzle size i.e. internal diameter. Based on the microstructure observations, the relationship between spray parameters and coating properties were analysed also with the MODDE data analysis software.
2 Background

2.1 Thermal barrier coatings

Thermal barrier coatings (TBCs) are a simple and proven method to protect hot section components, such as combustor liners, tiles, blades, vanes etc. in current gas turbine engines [1-3]. TBCs generally consist of the substrate (the component to be protected), a top coat and a bond coat which is sandwiched between the top coat and substrate. Due to the harsh working conditions in which TBCs operate, the functional properties of TBCs depends on the properties of the top coats to great extent. It is necessary that the TBCs possess low thermal conductivity, phase stability, erosion resistance and good adhesion to substrate [4]. Bond coat is mainly used to protect the substrate from oxidation and corrosion as well as to increase the top coat adhesion. Normally, M-CrAlY alloys are used as bond coat, where M is Nickel, Cobalt, Iron or alloys of these elements. Zirconia is usually used as top coat material because of its excellent properties that so far fulfil in the best way the requirements of TBCs. At temperatures around 1100 ºC, pure Zirconia undergoes a phase change that leads to volume change contributing to failure. Therefore, Yttria is widely used as a stabilizer mixed with zirconia which is commonly known as Yttria-stabilized zirconia (YSZ) [5] as the top coat. Figure 1 shows a cross section in TBC system.

2.2 Atmospheric plasma spray

Since the beginning of 1980s, Atmospheric Plasma Spray (APS) is widely used in manufacturing, especially in fabrication of TBCs because of its low cost and coating deposition efficiency [6]. Powder sizes ranging from 20 to 120 µm [7] are carried by a carrier gas and injected in the plasma jet where they are rapidly heated up and accelerated.

![Figure 1 Thermal Barrier Coating](image-url)
Suspension Plasma Sprayed Zirconia coatings properties - Background

A plasma gun is used to generate the plasma gas consisting basically of a chamber with one or more cathodes as well as anodes which are used to dissociate and ionise the plasma gas to form a powerful plume that is pushed out through a nozzle that constricts and increases energy density of the plasma jet. Plasma ions recombine to gaseous state due to their instability and release enormous thermal energy [8]. Temperatures over 8000K [9] will be generated during this process, which is sufficient to melt almost any material. Feedstock with the carrier gas is injected into the hot gas plume and is rapidly deposited on the substrate and is fully sintered thereby eliminating the need of any post-deposition heat treatment. The absence of heat-affected zones between the coating and substrate and the lack of component distortion along with excellent coating properties make APS a popular method of thermal spray.

As thick nanometre or sub-micrometre-sized coatings shows better properties, such as higher coefficients of thermal expansion, lower thermal diffusivity [7] etc., powders in nanometre and sub-micrometre are desired in thermal barrier coatings. However, because of the low weight and poor flowability [10] of powders in nanometre-scale, they cannot be injected in plasma plume directly. Also, powders less than 5 µm tend to agglomerate due to their electrostatic surface forces [11] which may lead to clogging in injectors. A new process to handle this problem is desired. One possible solution is to transport the powders with the help of a liquid carrier, the mixture of liquid and powders forming a suspension and the process is called suspension plasma spraying (SPS).

2.3 Suspension plasma spray

SPS is an emerging process technology, which uses a nanometre- or sub micrometre-sized particles dispersed in a liquid, generally water, ethanol or their mixture [12], as feedstock [13]. During the SPS process, once the suspension enter the plasma jet, the liquid carrier atomizes and then evaporates rapidly, so that the solid particles stick together, melt and impact the substrate to form the coating [12]. Due to its small droplets, ranges from 100 nm to several µm [14], SPS may allow one to obtain thin coatings.

Figure 2 Scheme of APS, picture adapted by Ref [8]
Suspension Plasma Sprayed Zirconia coatings properties - Background

(from 20 to 100 µm) [15] with much finer microstructures compared to APS. For instance, high segmentation crack densities can be obtained by controlling operating parameters which contribute directly to longer lifetime of the coatings [16].

There are two methods to provide the feedstock slurry - radial injection and axial injection, as shown in Figure 3. Radial injection (shown in Figure 3a) is a common way which use an external jet to inject the slurry along the radius of the torch [17]. In order to produce the required droplet which could penetrate the plasma jet and enter the centre of plasma plume, droplet size and velocity as vital parameters should be controlled strictly. On the other hand, axial injection (shown in Figure 3b) is directly injecting the feedstock into plasma plume by a co-axial injector. It overcomes the drawbacks of radial injection, but is more complex as the feedstock has to pass through the entire length of suspension feed lines. The size of the line also becomes a limitation and plasma gas flow rate, stand-off distance as well as suspension feed rate are the critical factors of axial injection [18,19].

Both injection methods involve the suspension being fed by a mechanical tank in order to obtain a more homogeneous particle size and velocity. The two modes of mixing the plasma gas and carrier liquid are shown in Figure 4. For internal-mixing (shown in Figure 4a), the carrier liquid is accelerated in a cylindrical chamber and then mixed with the plasma gas inside the nozzle at the end of the chamber. This mode provides a high level of mixing. On the contrary, external-mixing involves mixing of liquid and gas in front of the torch, shown in Figure 4b. Relatively more gas is necessary in external-mixing [13].

Figure 3 Schemes of injection mode a. radial injection b. axial injection

Figure 4 Injection nozzle, adapted by Ref [13] a. internal-mixing b. external-mixing
3 Experimental methods and materials

3.1 Materials

All coatings were deposited on same substrate material and same geometry i.e. round button samples (25mm in diameter and 6 mm thick). Feedstock materials and plasma gun details are shown in Table 1.

Table 1 Materials data

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Bond Coat</th>
<th>Substrate</th>
<th>Plasma Gun</th>
<th>Liquid carrier/suspension</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$ + 8 wt. % Y$_2$O$_3$</td>
<td>NiCoCrAlY</td>
<td>Stainless steel</td>
<td>F4-MB APS</td>
<td>Pure alcohol</td>
</tr>
</tbody>
</table>

3.2 Spray Details & Metallographic Preparation

Bond coat of all samples were plasma sprayed at PTC with the F4-MB APS gun made by Sulzer Metco. The samples were then sprayed with YSZ topcoats by SPS, using an Axial III Mettech gun and different spray parameters. There were 33 different type of topcoats sprayed in this experimental work. Table 2 shows the ranges of parameters and all the details of parameters are showed in Appendix A.

The sprayed samples were then cut using a diamond cutting blade in order to obtain cross sections for microstructure investigations. The specimens were mounted in low viscosity epoxy resin and polished using Buehler PowerPro 5000.

Table 2 Ranges of parameters

<table>
<thead>
<tr>
<th>Nozzle size</th>
<th>Total Gas Flow (l/min)</th>
<th>Power Level (KW)</th>
<th>Strokes</th>
<th>Suspension Rate (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>185-270</td>
<td>64-109</td>
<td>70-100</td>
<td>43.49</td>
</tr>
<tr>
<td>Medium</td>
<td>199-300</td>
<td>55.2-121</td>
<td>70-204</td>
<td>47.3-48.8</td>
</tr>
<tr>
<td>Large</td>
<td>185-300</td>
<td>53.1-147</td>
<td>67-100</td>
<td>48.4-48.8</td>
</tr>
</tbody>
</table>

3.3 Microstructural analysis and thickness measurement

Microscopy analysis was carried out using an optical microscope (OM) - OLYMPUS BX60M. Infinite Analysis (Software) was also used to choose twenty random locations in the entire cross-section at 100X magnification to measure the coating thickness and then calculate the average.

Scanning electron microscopes (SEM) are widely used in microstructural analysis due to their high resolution. For this analysis the SEM used was TM 3000 HITACHI with magnifications ranging from 100X, 200X till 6000X. Two pictures at 300X, one at 1000X and one at 5000X for taken each sample.
3.4 Porosity measurement

Image analysis is one of the reliable methods to test porosity. A large magnification is necessary in order to observe the tiny pores and voids. Normally, the sizes of pore and voids of SPS coatings ranges from a few microns to nanometers. Ten pictures of each sample were collected randomly across the entire cross-section in regions not close to the edges at a magnification of 5000X using the SEM. Aphelion 3.2 was used to analyse these pictures and calculate average porosity.

3.5 Roughness measurement

Average surface roughness values can change with different deposition conditions. Taylor-Hobson Surtronic 3 was used to test surface roughness in this work. It contains a drive moor which is moved across the surface. The moor contains at its end, a probe made of diamond which fluctuates with variations in surface configurations and thereby, the Roughness average (Ra) is calculated. For each sample a total of six readings were performed. Three readings were noted at two lines of motion of the probe.

3.6 SPS Parameters

In SPS experiments, all the parameters can be changed independently. Nevertheless, the relationship between different parameters are complicated. That means, in a certain condition, if some parameters are changed, it might lead to a completely different coating. Solution properties and characteristics, plasma torch power level and six other parameters are introduced in the following part.

3.6.1 Solvent

Different from APS, SPS use a suspension liquid carrier instead of a carrier gas to transport spraying material to the substrate. Therefore, a carrier liquid should satisfy the following conditions [20]:

1. Suspension should be stable enough to ensure the particles do not agglomerate.
2. Weight of suspension droplet should be light enough so particles are not strongly influenced by gravity.
3. Viscosity of suspension should be suitable to experiment.
4. Suspension evaporation should not extract too much heat from the plasma jet.

Thus water, ethanol or their mixture is used as a carrier liquid. However, different components of the suspension have a big influence on the viscosity of the plasma jet [12], particle velocities and the temperature [21]. According to existing literature, the total heat required to vaporize water is thrice that of ethanol [22]. That means, at the same SPS process conditions, temperature of particles in water-based solvents will be much lower than that of particles in an ethanol-based solvent.

The suspension is injected into the plasma jet via two modes. One is atomization and the other is the injection of a continuous jet. Liquid stream in jet injection is broken up by external forces of gravity depending on the geometry and velocity. On the other hand, an atomization injector needs an external energy source to break the liquid bulk. Different solvent properties like surface tension and viscosity lead to different particle sizes. Experiments show that the suspension size in water-based solvent is bigger than that in ethanol implying a greater difficulty in atomizing water-based solvents.

In this case, pure alcohol was used as the solvent.
3.6.2 DC Current & Power Level

The electrodes (i.e. anode/cathode pairs) mounted in the plasma gun are connected to direct current and used to generate a powerful arc to offer a plasma flow to melt the injection powders as well as accelerate the melted powder to the substrate. In other words, to some extent, the plasma flow equals the heat flow. Thus, the DC current has a big influence on the velocity, temperature and related thermal and physical characteristic of plasma flow [23]. In terms of the particles, the electrical energy produced by plasma jet is converted to be chemical energy and kinetic energy during this process. However, in order to keep plasma jet in proper operating condition, cooling water plays an important role in protecting the gun from overheating which will also take away part of the heat [14]. According to [23], heat losses increase proportionally with the current in arc and is slightly influenced by plasma gas flow rate, nozzle diameter and plasma gas composition. Therefore, plasma power equals the torch power minus the heat removed by the cooling water, which also equals the product of the effective torch voltage ($V$) and the arc current ($I$). In terms of definition of enthalpy, $h = P/\dot{m}$, where $P$ is the heat power, $\dot{m}$ is the gas flow rate, $h = V \ast I/\dot{m}$. The plasma gas velocity, $v$, is given by equation (2)

$$v = \frac{\gamma - 1}{\gamma} \cdot \frac{\dot{m} h}{\pi d^2 P_0}$$  \hspace{1cm} (2)

Where $\gamma$ is isentropic coefficient which determined by gas component, $d$ is nozzle diameter and $P_0$ is atmospheric pressure. It clearly shows the relationship between the arc current and the plasma velocity.

DC current not only influences plasma power, it also causes a continuously fluctuation of the rear of plasma jet at high voltage, which leads to major changes in the flight path of the particles. [23]. The instability of plasma jet results from the pressure changes in cavity, length of the arc, flow rate and the electric field [23].

During the process of SPS, DC current will also generate acoustic waves, which have an effect on injection liquid [23,24].

3.6.3 Suspension Rate

Suspension rate means the flow rate of suspension. As previously mentioned, due to the different injection modes, the influence of the spray parameters are different. Suspension rate has two effects on radial injection SPS, one is on powder passing through the plasma gas and into the centre of plasma flow and the other one is energy used to vaporize the liquid and melt the YSZ [25]. As for axial injection, there is a coaxial internal injection at the end of the plasma gun and since the suspension is already in the centre of plasma flow, the suspension rate influences the energy of vaporization the most.

At a proper feed rate, suspension powder could be fully heated and melted in plasma gun. With the increase of feed rate, the powder do not have sufficient time to be heated and consequently the powder temperature decreases [26] leading to a decrease in conversion of chemical energy, an increase of the number of unmelted powder particles and contributing to slightly lower particle velocities.

3.6.4 Nozzle Diameter

The diameter size of nozzle largely affects the coating density. Experiments show that at the same plasma gas flow rate, coatings produced by small nozzles have a higher density than those produced with larger ones [14]. As shown in equation (3)
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\[ \rho_{\text{coating}} = \frac{m}{V} \quad (3) \]

Where \( m \) is the mass of coating and \( V \) is the volume of coating which equals coating thickness multiplies the surface area. Lower density means thinner coating with less pores or cracks.

3.6.5 Gas Flow Rate

Gas flow rate has influence on torch power and leads to changes in coating density. From literature study, an increase of the gas flow rate contributed to increasing the torch power and plasma velocity [14]. However, there exists a limit for changes in density beyond which increase in gas flow rate does not increase coating density.

3.7 Auxiliary Equipment

With the development of science and technology, robots have replaced involvement of human work in many areas, especially in harsh working environments. Due to the hot and noisy surrounding of SPS which is not safe for operators, a six-axis robot shoulders the responsibility of holding a plasma gun. A small oscillation can cause big changes in particle trajectory, which may result in the powder escaping from the centre and lead to undesirable results. The stabilization of plasma gun is essential to the whole SPS process.

Movement of plasma gun is in one or two dimensions. Turntable with rotational symmetry is used to hold the substrates to make sure the angle of specimen relative to plasma gun is desirable.

3.8 Experimental data analysis software

3.8.1 MODDE 10.1 and DoE

MODDE 10.1 is a nice software to set up the design of experiments (DoE) and analyse the experimental results produced by UMETRICS. DoEs, based on statistics, are usually used to design parameters step by step in order to have the optimized experimental cases, however, it is also possible to design all factors. On the other hand, it is utilised to study the relationship between different factors as well. In this case, DOE was used to identify the most important process parameters: total gas flow rate, power level, stroke and suspension rate. And other operating parameters were constant.

MODDE 10.1 will analyse the mathematic relationships between factors based on its powerful data-base. In this work, MODDE 10.1 was used to test which parameters will influence TBC coating properties and predicts model validity.

3.8.2 Aphelion 3.2

In suspension plasma spray coatings, the pore dimensions vary from a few microns to nanometres and it may not be detected directly. With the help of higher magnification SEM, such small pores could be detected and Aphelion 3.2 is utilized to analyse images to calculate coating porosity. Total porosity, consisting of globular pores and cracks were tested. However, multiple measurements showed that the porosity analysed by Aphelion 3.2 changes with the change of grayscale threshold values, brightness and contrast of sample images. After many times testing, suitable threshold values were selected to obtain correct results.
3.9 Sources of error and error intervals

This thesis focuses on five factors that may have a major influence on ZrO₂ top coat. 33 samples were deposited. Due to the small number of samples of same type, the results may be lacking in repeatability. There also exists some error during experiments because the processes were not completely automated. In addition, since the variables were measured manually, some inescapable inherent errors coming from the operator.
4 Results and Discussion

4.1 Results analysis from MODDE

Figure 5 shows the scatter plot figure from MODDE 10.1. Green markers are responses - coating properties, and the blue ones are factors - spray parameters. A big distance of

![Figure 5](scatter plots in PLS for a. small nozzle b. medium nozzle c. large nozzle
(Ave: average thickness; av2: average roughness; por: porosity; den: crack density. Tot: total gas flow; Pow: power level; Str: strokes; Sus: suspension rate)
the factor markers from the horizontal axis shows the large influence of that factor on the response.

PLS is short for partial least square, which finds a linear regression model with predicted variables and observables.

**Figure 6** Fit and prediction of models for a. small nozzle b. medium nozzle c. large nozzle
Figure 6 shows the model fit and prediction of coating properties. R2 shows the model fit. If R2<0.5, that means that the model is with low significance. Q2 shows an estimate of the future prediction precision. The higher values of Q2 means greater model.

According to Figure 5 and Figure 6, following conclusions can be drawn:

1. There are two models in this work: one is for small and large nozzle, the other is for medium nozzle. This may be because the pressure changed with different nozzle sizes.

2. Coefficients plot are used to support the conclusion about the importance of factors. But the fit and prediction of models are not taking the scatter plots fully into account.

3. Strokes mainly influence on coating porosity.

4. Power level have a significant effect on crack density and coating thickness in both models. For small and large nozzle, total gas flow rate also have a slight influence on these properties.

Overall, the models are only valid within the design region analysed, and extrapolation may add unpredictable and uncertainty of the results.

4.2 Microstructure Analysis

Figure 7 shows the microstructure SEM images of the coatings produced with small nozzle (Figure 7a, 7b and 7c), medium nozzle (Figure 7d, 7e and 7f) and large nozzle (Figure 7g, 7h and 7i) in high and low power level.

As can be seen in Figure 7, vertical cracks appear in every investigated coating. They are important features in SPS TBC. During the deposition, hot particles arrive on the substrate and generate high compressive stress. High temperatures along with high
Figure 7 Microstructures of samples deposited with small nozzle (a, b, c), medium nozzle (d, e, f) and large nozzle (g, h, i)
compressive stress lead to time-dependent stress release [27]. Due to the absence of heating system in substrate, the deposited powders enter into a cooling stage where compressive stress finally turn tensile in nature. In-plane thermal tensile stress generated during the deposition is so large that it can segment the biaxial deposition coating easily, therefore, the vertical cracks also are named segmentation cracks. It runs from the bond coat to the surface of the top coating and is longer than half the thickness of the top coating. Vertical cracks reduce the thermal conductivity to large extents in certain situations. Some literatures also revealed that the strain tolerance increased with the high density vertical cracks [28]. Overall, the vertical cracks improve coating durability. As the driving force of vertical cracks is thermal tensile stress, substrate temperature plays an essential role in generating segmentation cracks. Therefore, the power level of the torch is the most important factor. High power level contributes directly to a high particle temperature and leads to high vertical cracks density (VCD), which equals to the number of vertical cracks divided by the cross-section length. Researches also showed that the passage thickness and the thickness of each lamellae also have a significant influence on the vertical cracks. With the passage thickness increasing, vertical crack density shows a growing trend [29].

From the SEM images, in terms of small nozzle, TBC deposited in high power level (Figure 7a) shows much more significant and higher vertical cracks density compared with TBC deposited in both medium power (Figure 7b) and low power level (Figure 7c). Similar situation occurs in medium and large nozzle as well. Table 3 shows the segmentation cracks density for the images shows in Figure 7. Figure 8 shows the result of the VCD of all the samples. According to Figure 8, it can be concluded that the higher the power level leads to a higher the VCD.

Table 3 VCD for samples in Figure 7

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>7a</th>
<th>7b</th>
<th>7c</th>
<th>7d</th>
<th>7e</th>
<th>7f</th>
<th>7g</th>
<th>7h</th>
<th>7i</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCD (item/mm)</td>
<td>7.85</td>
<td>6.64</td>
<td>3.62</td>
<td>5.74</td>
<td>5.13</td>
<td>1.82</td>
<td>9.35</td>
<td>3.78</td>
<td>4.08</td>
</tr>
</tbody>
</table>

Figure 8 testing result of vertical cracks density
Photomicrographs in Figure 7 show that another kind of cracks are also present that originate from the vertical cracks and are parallel to the substrate. They are named branching cracks. As mentioned above, vertical cracks are generated by in-plane biaxial thermal tensile stress. When this stress is unbalance, branching cracks appear. Branching crack is the most undesirable microstructure of SPS coating. It will lead to coating failure and decrease coating durability.

Previous research shows that, particle size has a big effect on particle trajectory [30]. Particles in 40µm have a vertical velocity, 400m/s, to the substrate when the stand-off distance is 1cm. With the same spray process, particles in 5µm will have a small velocity component parallel to the substrate, and its vertical velocity component is 350m/s. Therefore, there will be a small excursion for the particle trajectory. In addition, with the particles size decrease, velocity component parallel to the substrate grows fast and the trajectory of particles whose diameter are less than 3 µm has a big excursion compared to particles of size 40 µm and 5 µm. At the same time parallel and vertical velocity components decrease considerably. That means, during the deposition, droplets arrive at substrate in liquid state. But different size particles deposit in different locations. Big particles will follow the main stream and hit the substrate and transfer the vertical velocity to the velocity which is parallel to the substrate and form the coating. On the other hand, small particles will deposit at other positions leading to formation of microprotrusions. As coating thickness increases the height of the micro-protrusions grows in a columnar fashion and eventually larger particles can no longer come in contact with the bond coat, they deposits on precisely deposited coating. Some unmelted and resolidified particles could not fully contact with previously coatings and lead to generation of inter-pass pores. High particle velocities are the main reason behind generation of columnar feature and inter-pass pores are generated because of torch power level.

In SPS process, as already known, powder velocity is mainly controlled by gas flow rate and torch power level. Comparing the images shown in Figure 7 a, b, c, for small nozzle size, there are significant columnar features in Figure 7a, and the columnar feature in Figure 7b is not as clear as that in 7a. There are no clear columnar features in 7c. This confirms the predictions.

Columnar feature is desirable microstructure in TBC; because, due to the columnar grains, the heat will not transfer along the inter-pass pores, consequently the thermal conductivity will be lower. However, inter-pass pores are not desirable as they can promote branching cracks and thus shorten the lifetime of the coatings. They may also decrease the formation of vertical cracks.

### 4.3 Thickness

TBCs are the result of the stacking of particles. Therefore, the deposition efficiency is the factor which effects the coating thickness. Due to the principle of coating forming, the coating grows from the substrate perpendicularly, the higher particle velocity, the higher deposition efficiency.

Figure 9 shows the results for the thickness measurement. For both models, with the increase of the power level, the average thickness shows a growing trend. But, the gradients are different – that of medium is much larger than small and large nozzles. That is because, from the analysis of MODDE, in this case, in small and large nozzles, power and gas flow rate have co-effects on coating thickness. Suspension rate of the large nozzle also influences the coating thickness. That may be because, for the large nozzle, the angle of plasma plume is larger than small nozzle, therefore, a number of particles
will not be deposited on the coatings. High suspension rate ensures that more particles deposited on the substrate. However, in medium nozzle, the coating thickness is determined by the power level of torch. That may be because, in the medium nozzle, gas flow rate is not a significant factor and not affect the particle velocity greatly.

4.4 Porosity Measurement

Porosity is one of the most desirable properties for TBCs. Air, as a good insulation material, exists in the pores and voids and considerably decreases the thermal conductivity of the coatings. Porosity in SPS could be controlled during different spray process parameters. In APS, porosity ranges from 15% to 20%, but in SPS, it could be much higher. However, even though a higher porosity is better, it should be in a certain range; because materials with high porosity will be more friable and will fail earlier. The SPS coatings consist of three typical “granular” morphologies. They are [15,31]:

1. Well molten particles (W)
2. Unmolted particles (U)
3. Small spherical grains which have resolidified (R) before they arrive on substrate.

Moreover, Tingaud et al. [31] showed that a higher (U+R)/W ratio corresponds to the higher porosity of the coating.

Figure 9 coating average thickness
During the deposition process, the well molten particles will form the flattened lamellae which will connect with the previous deposited coating, the unmolten particles show the shape of the feedstock and the resolidified particles show a spherical shape. In terms of the resolidified particles. For both the unmolten particles and the resolidified particles, the shapes of them will be higher than the flat and lead to shadows as a result of the voids/porous. Therefore, the more particles sprayed on the substrate means the higher porosity.

For both medium nozzle model and small and large nozzle model, strokes, the number of the depositing layers is the main factor which affects the porosity. The more strokes, the higher porosity in the coating as shown in Figure 11. According to previously mentioned, samples deposited by large nozzle, sprayed in same number of strokes, have almost the same porosity. That means the stroke is the only factor affecting the coating porosity. However, in terms of the samples with the same stroke, they have different porosity. That is because, other operating parameters also have influences on the porosity. Results from MODDE show that, suspension rate in small nozzle is the other reason behind porosity. Meanwhile, suspension rate and total gas flow rate have slight co-effect on it as well. Figure 11 shows the variation tendency of porosity with the change of suspension rate. In terms of model with small nozzle, the porosity shows a small raise but for medium nozzle, compared with the coating sprayed in a suspension rate in 46 L/min, porosity of mostly samples decreased. That may be because, of the small nozzle, the plasma plume velocity relatedly lower than that of the plasma plume generated by medium, therefore, with a certain cooling rate (in air), the percent of resolidified particles increased. Hence, the more particles injected in plasma plume, the
larger number of resolidified particles in small nozzle. In contrast, due to the less resolidified particles, the porosity of coating produced by medium decreased. In addition, according to Figure 10, when the number of strokes was the same, coating deposited by small nozzle had larger porosity than that produced by nozzle in large and medium size.

4.5 Roughness

In this work, all the bond coats were deposited in the similar conditions. Meanwhile, literature shows that the substrate surface roughness is independent of the coating roughness, and the coating surface roughness could be controlled by operating parameters and the particle sizes [26].

As mentioned in Chapter 4.2, the location of deposition relies on the velocity and the size of particles. And the previously deposited particles would affect the later ones, which means if the later particles were deposited on the position where the smaller had deposited, there would be a protuberance, which would lead to the variation of surface roughness.

As previously mentioned, the velocity of particles were controlled by the power level. Therefore, it could be concluded that power level is a big factor which influenced the coating roughness.

Results for the experiments are shown in Figure 12. From the results, it can be seen that in small and large nozzle, with the increasing of power level, coating roughness increases. In terms of the medium nozzle, the situation is not sure, because there were no samples made in as large power level as those which were deposited with small and large nozzle, however, surface roughness goes down with the increase of power level which range from 55.2KW to 121KW. From MODDE, coating roughness is influenced by suspension rate and total gas flow rate as well as strokes.
Figure 12 experiment result of coating roughness
5 Conclusion

In this work, three nozzle size and four operating parameters were tested as regard their influence on thermal barrier coatings sprayed by suspension plasma spray. Coating thickness, roughness, microstructure and porosity were analysed. Thirty-three different samples were produced for this study. Results, analysed by MODDE, showed that coating properties were determined by operating parameters and in different models, operating parameters play different roles on coating properties.

Overall, it could be concluded as following:

1. Different nozzle sizes show different mathematic models in SPS because of the pressure changed by nozzles. Small nozzle and large nozzle showed the similar result in this work but coatings deposited with medium nozzle showed different coating porosities.

2. For small and large nozzle, power level was the dominant factor, and gas flow rate seemed to have effect on the particle velocity which in turn has a big influence on coating thickness, roughness and coating microstructures. Coating thickness and roughness rise up with the increase of power level. Columnar structures and inter-pass pores appear when the spray process has a high power level and gas flow rate. In terms of the vertical cracks, they are one of the most typical microstructure of SPS coatings, and are generated because of the high thermal stresses induced during spraying. Therefore, high power level is the factor behind high density of vertical cracks. Strokes, the number of the coating deposited layers, are the main reason of porosity. The more layers deposited, the higher porosity. In small nozzle, the increase of suspension rate could increase porosity slightly as well.

3. For the medium nozzle, it was a different model compared with small nozzle and large nozzle model. The power level determined the coating thickness and coating structure. High power level resulted in high vertical density and thick coating thickness. Coating porosity grew with the deposited layers – strokes to large extend. Coating roughness was influenced by the suspension rate and gas flow rate as well as strokes.

5.1 Future Work and Research

In this thesis work, coating thickness, roughness, microstructure and coating porosity were tested. However, due to the amount of samples was not enough, the suggested test plan should be as $2^4+3=19$ samples for each nozzle size, fifty-seven in total, which is a “full factorial design with three center point”. In order to have the repeatability, three samples made with medium values is necessary. This design supports a linear model approach and is a base for a possible future response surface model for which a couple of additional experiments is needed.

Coating thickness, roughness, microstructure and porosity were important properties, some more coating properties should be tested, such as coating’s thermal conductivity, permeability and so on.
5.2 Generalization of the result

All the results generated in this thesis can be generalized because all the analysis were based on existing literature and experiments. Also, the large experimental sample number was also the reason that results were generalized.
6 References


[34] B. Liu and Y. Zhang, "La0.9Sr0.1Ga0.8Mg0.2O3–δ sintered by spark plasma sintering (SPS) for intermediate temperature SOFC electrolyte," Journal of Alloys and Compounds, vol. 458, no. 1-2, p. 383–389, 2007.

## A. Appendix

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### B. Appendix

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