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# Role of Particle Injection Characteristics on Coating Microstructure of Plasma Sprayed Zirconia

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Yttria-stabilized zirconia (YSZ) powders (50 – 100 μm in diameter) have been used to prepare plasma-sprayed thin ceramic films on the stainless steel and nickel sheets employing non-equilibrium plasma spray technology at atmospheric pressure. The dependency of microstructure of coatings on initial powder characteristics was investigated. Furthermore, effects of various plasma spray conditions on microstructure, crystallite size, phase content of the coatings have been evaluated. Plasma spray zirconium oxide coatings deposited onto different substrates have been characterized using optical microscope, scanning electron microscope (SEM) and X-ray diffractometer (XRD) for study of microstructure and phase analysis as a part of a process optimisation study. The deposits characteristics were compared with the processing parameters and revealed that the deposit characteristics strongly depended on the in-flight particle parameters. The coating sprayed using finer powder displays better structural characteristics than the counterpart sprayed using coarse-grained powder feed. The density of the film increases with the spray temperature. The crystallite size of the film also exhibits a strong dependency on the spray conditions. It was demonstrated how the spray regime affects the thickness, density and porosity of the obtained films.
*Keywords*: Films, microstructure, plasma spraying, $ZrO_2$.

## 1. INTRODUCTION

The increasing requirement for high technology materials with specific properties in various types of environments has dictated that these materials possess near-surface properties different from its bulk values. It concerns also thin ceramics films, deposited on various surfaces. Among many processing techniques, a plasma spray is a quick and inexpensive process for fabricating thin yttria stabilized zirconia (YSZ) film used for SOFC applications [1]. It was established, that a lot of intergranular defects are introduced in the film by plasma spraying process, so the proper post-treatment is needed to make the YSZ film to be full dense [2].

In this work we describe the structures of YSZ films resulting from different particle injection characteristics employing non-equilibrium plasma spraying technology at atmospheric pressure. These were applied in order to determine powder size, plasma jet parameters, distance from plasma outlet to coating surface and powder injection place influence on the deposited films.

Mentioned above spray parameters mainly influence the coating microstructure and film adhesion [3]. For this study we report some results obtained for plasma sprayed YSZ films on steel and nickel alloy substrates using two different plasma torch shapes – Laval-like contour and cylinder. The results reported here represent a first attempt to obtain film with more dense structure. The aim of this work was to study a role of particle injection characteristics on the coating microstructure of plasma sprayed zirconia deposited on the sheets employing non-equilibrium air plasma spraying technology at atmospheric pressure.

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## 2. EXPERIMENTAL

A special test bench with long operation time and stable outlet plasma jet parameters was built [4, 5]. It consists of these main systems: electricity supplies, gas supply, cooling system and operation control and data monitoring system. Continual date monitoring of operating plasma torch allows the test bench functioning. Schematic view of the experimental set-up is shown in Fig. 1.

The average outlet jet temperature and velocity were determined from heat balance. The capacity of plasma torch, mass flow of gases, cooling water and its temperature were measured and gas enthalpy was calculated. Gas temperature and velocity were determined numerically using gas property data for the "frozen" state of gases. Local jet temperature and velocity distributions were measured by means of a cooled calorimetric probe [6].

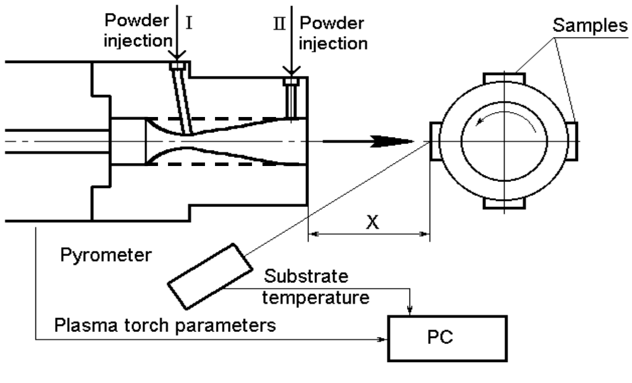



**Fig. 1.** Experimental set-up

The plasma torch was constructed so that powders injection could be provided internally or externally. Internal powder injection was arranged at different positions (Fig. 1). This allows feeding of high melting materials directly into plasma core, expending in this way spraying optimum conditions for different materials.

Typical spray parameters of the plasma torch used in the present case were: power supply ($P$) - 35 – 40 kW, arc current ($I$) - 120 – 200 A, voltage ($U$) - 225 – 300 V, total gas flow rate ($G$) - 4.9 g/s (the main gas flow rate throw plasma torch - 2.65 g/s, additional - 2.25 g/s, hydrogen - 0.12 g/s). Average plasma temperature in the powder injection place – 3300 – 3700 °C, outlet plasma temperature – 2700 – 3300 °C, the average velocity - 650 – 1350 m/s, the working gas - air. Table 1 summarizes the experimental conditions.

**Table 1.** Spraying parameters of YSZ film

| Regime | L | C |
|---|---|---|
| Exit shape | Laval contour | Cylinder |
| $P$, kW | 45 | 47.5 |
| $G$, g/s | 3.65 | 3.65 |
| $G(H_2)$, g/s | 0.1 | 0.1 |
| $T$, °C | 3370 | 3180 |
| $x$, mm | 20 – 100 | 20 – 100 |
| $v$, m/s | 1120 | 980 |

Two shapes of anode exit mode were used for thin film deposition. One of them was Laval-like exit contour. The powder was injected into the critical nozzle diameter (regime L). Laval-like exit contour results a controlled expansion of the plasma core and leads to very high jet velocities. In this case the outlet plasma jet has extended hot core, delay the detrimental influence of cold surrounding gas. The other was a cylinder (Fig. 1, dashed line) 80 mm in length and 7 mm in diameter. In this case there was longer plasma – powder particle interaction time (regime C) and as result better particle-melting conditions.

The substrates were mounted on a cylindrical fixture and rotated around its own axis. The plasma torch mowing in horizontal direction creates the coating surface.

The objective of the present study is thus to investigate the effect of particle injection characteristics on the structure of plasma-sprayed YSZ film. Major characterization techniques included optical and scanning electron microscopy (SEM) and X-ray diffraction (XRD). The microstructure was characterized using an SEM (JSM 5600). Phases of the various calcined powders as well as sprayed films were analyzed by X-ray diffractometer (DRON-6) with Cu $K_\alpha$-radiation. The mean crystallites size was estimated from integral width of the diffraction peaks (111) of YSZ by WINFIT program [7]. The bulk densities of sprayed films were determined from their dimensions and weights according to the Achimedes principle. The film thickness was evaluated by cross-sectional scanning electron microscopy (SEM) observation. Specimens for cross-sectional microscopy were prepared by mounting the specimens in epoxy resin, followed by polishing through 0.05 μm alumina.

## 3. MATERIALS

A commercial yttria stabilized zirconia powders (10 mol % $Y_2O_3$) with particle size 50 – 100 μm were used in this work. Table 2 presents the characteristics of the started powders investigated in the present study. After being dried and calcined at corresponding temperatures for 2 hours, the resultant powders were used to form plasma sprayed coating on various substrates.

**Table 2.** Properties of YSZ powders for plasma spraying

| Powder type | Particle size (μm) | Heat treatment (°C) |
|---|---|---|
| YSZ-1 | 63 – 100 | – |
| YSZ-2 | 50 | – |
| YSZ-3 | 50 | 700 |
| YSZ-4 | 50 | 900 |
| YSZ-5 | 63 – 100 | 900 |

Polished stainless steal and nickel sheets were used as the substrate material. Prior to plasma spray, the substrate surface was hand-polished to 0.05 μm finishing. All substrates were cleaned by acetone and dried in air before they were used. To obtain a uniform coating, the substrates were placed on the fixture, which could rotate during plasma spray, 20 – 100 mm away from the exit of the torch, and heated by a plasma flame. The substrate temperature was controlled by the optical pyrometer. The thickness of the steel and nickel substrates was 100 and 50 μm, respectively.

## 4. RESULTS AND DISCUSSION

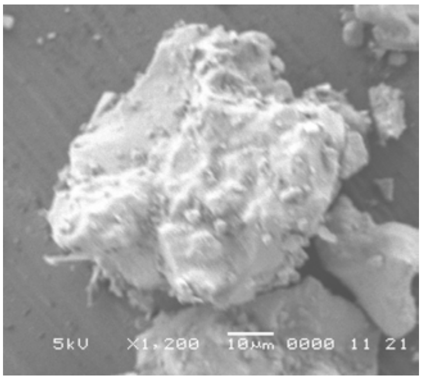
### 4.1. Powder characterization

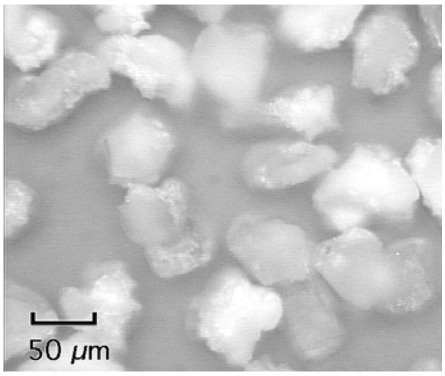
Morphologies of the various initial and heat-treated powders as well as plasma-sprayed powders are shown in Fig. 2 and Fig. 3. The initial powder YSZ-1 is in the form of agglomerates with wide grain size distribution having average crystallite size 22 nm. The powders YSZ-1 and YSZ-2 are analogous and differ only in size. As shown in the micrographs, all the heat-treated (50 μm) powders are irregularly shaped and appear quite similar. By the XRD data all of them have a crystalline cubic phase.

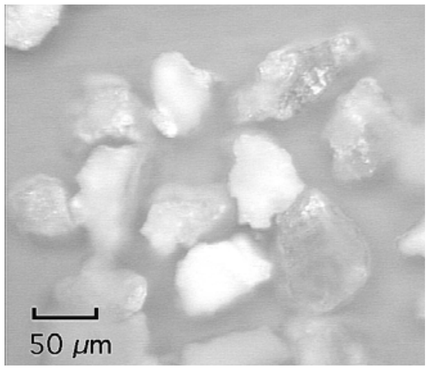
SEM and optical observations of powders used have revealed a significant morphology differences between two spraying regimes. During plasma spraying by regime C, all size powders were completely melted and spheroidized. During spray process by regime L, only some of larger size powders are also spherical or ellipsoidal; others are partly melted and have irregularly shaped surface morphology. Fig. 3 reveals the morphology of plasma sprayed YSZ powder as observed in a scanning electron microscope. By the data obtained it was determined, that during the plasma spraying process by regime L, the powders are heated at lower rate in this shape of plasma torch.

### 4.2. Characterization of as-sprayed films

A Scanning Electron Microscope (SEM) was used to determine the films morphology and their thickness. It was determined (Fig. 4), that film properties strongly depend on started powder characteristics when powder is injected into Laval-like exit contour (L). Probably, the calcined grains impact the substrate with a higher momentum, and finally form a denser film. By the data obtained, it was

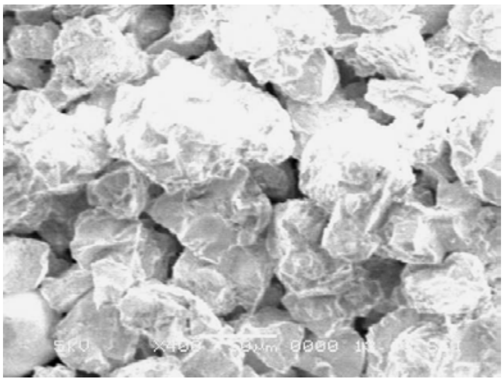




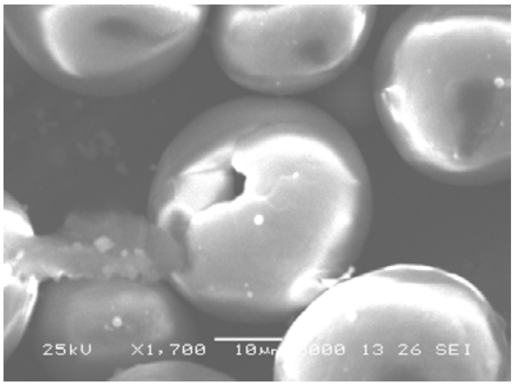



YSZ-2 YSZ-3 YSZ-4

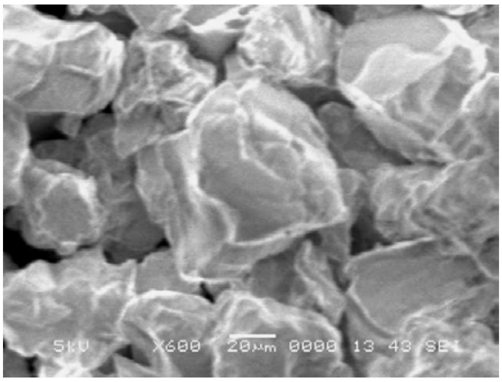
**Fig. 2.** The morphologies of starting powders



a

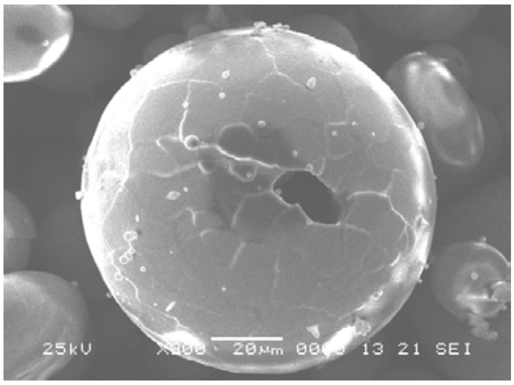



b




c

Regime L




d

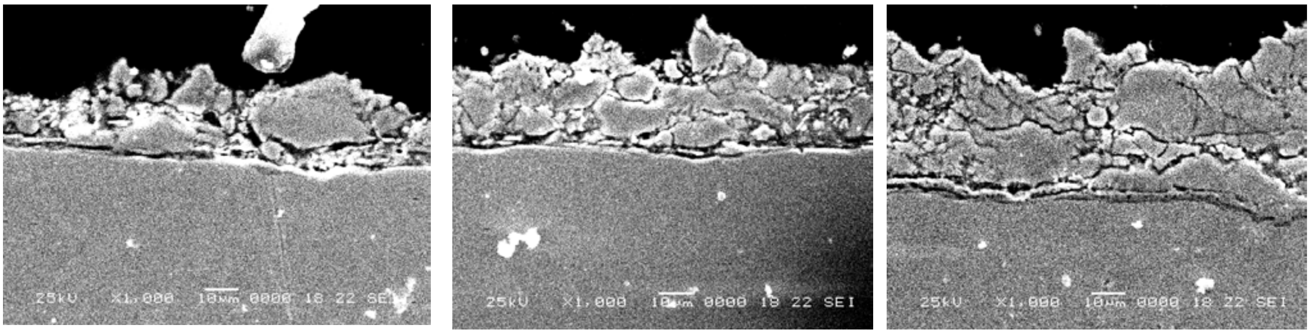
Regime C

**Fig. 3.** SEM micrographs of the powder particles YSZ-2 (a, b) and YSZ-1 (c, d) after passing through the plasma jet as a function of the processing regime

determined, that this regular is not characteristic to plasma spray regime C.

Despite different thermal regimes of initial powders, the morphology of all films is similar, as shown in Fig. 4. Randomly distributed pores of different sizes are also observed in all coatings. Table 3 shows the effect of thermal treatment of started powder on bulk densities and porosity of the YSZ films sprayed by regime L. It results that the highest density value (4.843 g/cm$^3$) is attributed to film obtained from powder (50 µm) calcined at 700 °C for 2 h. The films obtained from heat-treated powder appear to be denser compared with non-treated powder.

By the data obtained with cylinder-shaped plasma torch (regime C), the films are characterized by more dense structure, low porosity (Table 4). This might be interrelated with longer plasma-powder particle interaction time and better particle-melting conditions. The polished cross-section of the films shows that pores size is ≤ 3 µm.



YSZ-3 YSZ-4 YSZ-5

**Fig. 4.** Effect of heat treatment of started powder on plasma-sprayed YSZ film morphology. Regime L, spray distance 55 mm, spray duration 60 s

**Table 3.** Bulk density and porosity of the YSZ films sprayed by regime L ($P$ - 49 kW, $t$ - 60 s, $x$ - 55 cm) versus started powder type

| Powder type | Bulk density (g/cm$^3$) | Porosity (%) |
|---|---|---|
| YSZ-1 | 2.555 | 55.18 |
| YSZ-3 | 4.843 | 11.64 |
| YSZ-4 | 3.606 | 36.74 |
| YSZ-5 | 3.706 | 34.98 |

**Table 4.** Bulk density (g/cm$^3$) of the YSZ films sprayed by regime C versus started powder size and power supply

| Powder type | 33.6 kW | 45 kW | 48 kW |
|---|---|---|---|
| YSZ-1 | 4.82 | 4.986 | – |
| YSZ-2 | 4.972 | 5.135 | 5.245 |

According to the data of XRD analysis no distinct peaks except for cubic zirconia are found from X-ray diffraction patterns (Fig. 5).

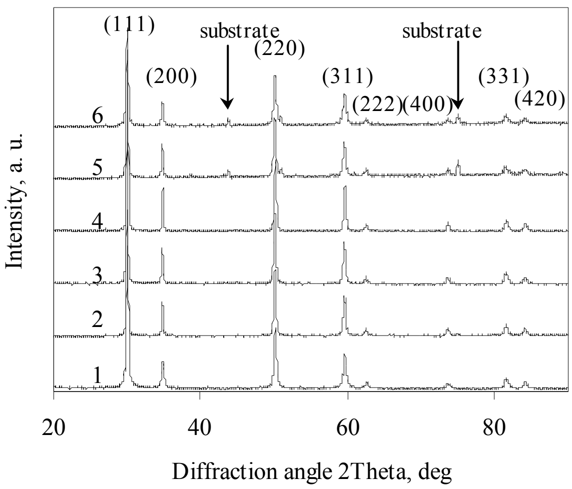



**Fig. 5.** The XRD patterns of YSZ: 1 – initial powders (YSZ-1), and 2 – 6 – plasma-sprayed films obtained by regime C (2 – YSZ-1, 3 – YSZ-2) and regime L (4 – YSZ-1, 5 – YSZ-3, 6 – YSZ-4)

The crystallite size of the films obtained from calcined powder by regime L (Fig. 6, column 2) is not very differing from initial powder (23 nm). It depends on the powder treatment (Fig. 6, column 2 - YSZ-4 and column 3 - YSZ-3). Crystallite size of the films sprayed by regime C ($x$ - 70 mm) increases up to 33 – 39 nm in spite of the type of powder used (Fig. 6, columns 4 – 6: 4 - YSZ-1, 5 – 6 - YSZ-2).

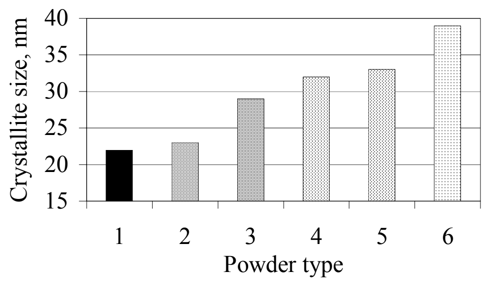



**Fig. 6.** Effect of plasma-spay regime and powder type on crystallite size of obtained films: 1 – initial powders (YSZ-1), 2 – 3 – regime L and 4 – 6 – regime C

The cross-sectional SEM micrographs showed that the thickness of all coatings was roughly between 10 and 60 μm. The rather large deviation in thickness is quite common for YSZ films sprayed by regime L, using thermal treated powders. Fig. 7 shows the effect of spray distance on the thickness of YSZ film obtained by regime L. It was noticed, that the optimal spray distance for both regimes L and C is 70 mm.

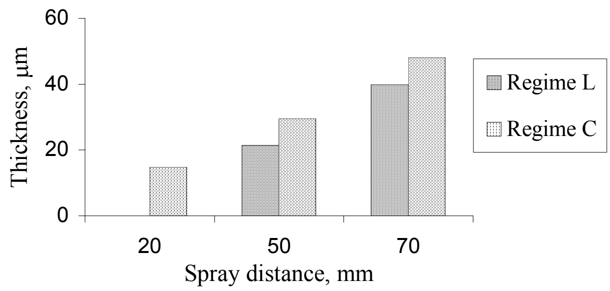
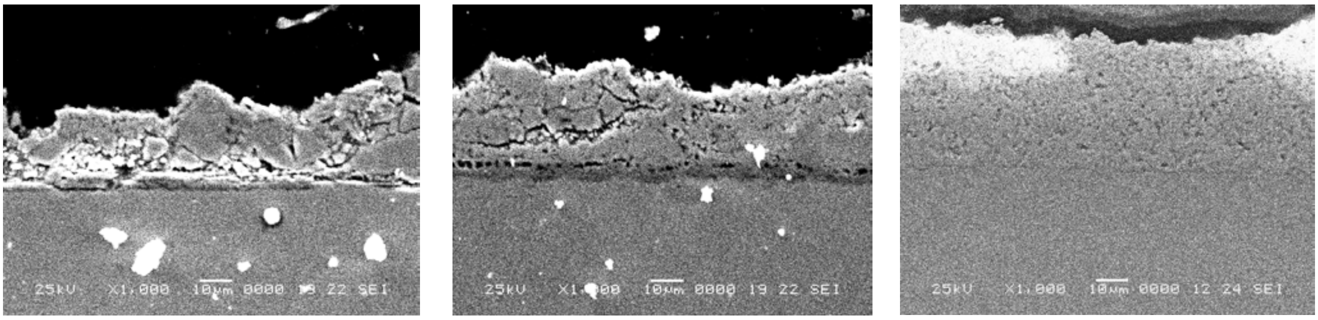



**Fig. 7.** Influence of spray distance on thickness of plasma sprayed YSZ film using started powder YSZ-2

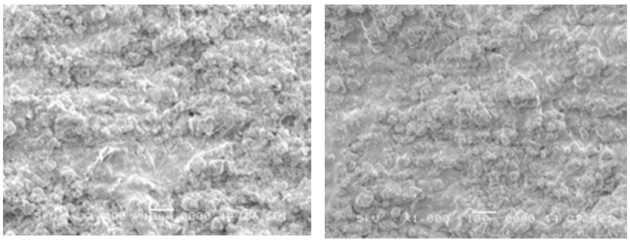
The thickness of YSZ films is slightly heterogeneous and differs from 60 μm in thickest region up to 30 μm in thinnest region. Usually, the thickest areas are formed from the powder with worse degree of melting [2].



$P$ – 33.6 kW ($T$ – 2661 °C) $P$ – 42.6 kW ($T$ – 2820 °C) $P$ – 48 kW ($T$ – 3331 °C)

**Fig. 8.** Influence of $P$ on plasma sprayed YSZ film properties. Regime C, $x$ - 70 mm, started powder YSZ-2

For many of the conditions investigated in this work, it was observed, that films deposited at the higher plasma power (45 – 48 kW) are qualified by finer and reduced porosity and increased density (Fig. 8). Typical plasma-sprayed structural defects and randomly distributed pores could be observed on the cross sections of all coatings.



a b

**Fig. 9.** SEM micrographs of surface morphology of YSZ films sprayed by regime L (a) and regime C (b)

Fig. 9 shows the surface morphology of typical plasma sprayed YSZ coating produced by two different regimes. The surface of the film obtained by regime C is more smooth and flat. The surface region consists mainly of small grains of a few micrometers in size.

## 5. CONCLUSIONS

In this work a role of particle injection characteristics on the coating microstructure of plasma sprayed zirconia was studied employing non-equilibrium air plasma spraying technology at atmospheric pressure. YSZ films have been deposited on steel and nickel alloy substrates by plasma spray technique using two different regimes of plasma spray deposition technique according different plasma torch shapes.

It is concluded that all initial powders were irregularly shaped and appeared quite similar in spite their heat treatment at 700 and 900 °C. As-sprayed powders were completely melted and spheroidized only during plasma spraying with cylinder-shaped plasma torch.

The present study showed the changes of the structure of the YSZ films with the changes of spray regimes. The data indicate that the regime of thermal treatment of started powder significantly affects the structure of YSZ films sprayed by regime L. The highest density value and low porosity is attributed to the film, obtained from started powder YSZ-3, calcined at 700 °C for 2 h. By the results, the YSZ films deposited with cylinder-shaped plasma torch (regime C) are characterized by more dense structure and increased crystallite size. The density of films increases with higher spray temperature (power supply). The films sprayed with a finer particle size are characterized by relatively improved structure.

Based on the results obtained, it can be deduced, that the variation of plasma parameters (especially plasma torch shape, plasma power and spray distance) has a great influence on the properties of YSZ films.

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**REFERENCES**


1. **Singhal, S. C.** Advances in Solid Oxide Fuel Cell Technology *Solid State Ionics* 135 2000: pp. 305 – 313.
2. **McPherson, R.** The Relationship between the Mechanism of Formation, Microstructure and Properties of Plasma Sprayed Coatings *Thin Solid Films* 83 1981: pp. 297 – 310.
3. **Chen, D. J., Mayo, M.** Densification and Grain Growth of Ultrafine $Y_2O_3$-$ZrO_2$ Ceramics *Nanostructured Mater.* 2 1993: pp. 469 – 478.
4. **Valincius, V., Valatkevicius, P., Pranevicius, L. L.** Employment of Electric Arc for Cover Deposition *Electronics and Electrical Engineering* 1 (19) 1999: pp. 26 – 29.
5. **Ambrazevicius, A.** Heat Transfer during Quenching of Gases. Vilnius, Mokslas, 1983 (in Lithuanian).
6. **Fincke, J. R., Swank, W. D., Snyder, S. C., Haggard, D. C.** Enthalpy Probe Performance in Compressible Thermal Plasma Jets *Rev. Sci.* 64 1993: pp. 3585 – 3593.
7. **Krumm, S.** An Interactive Windows Program for Profile Fitting and Size/Strain Analysis *Materials Science Forum* Vol. 228 – 231: pp. 183 – 188.