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# Mechanical properties and oxidation behaviour of plasma sprayed functionally graded zirconia–alumina thermal barrier coatings

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**Abstract**

The microstructures of thermally sprayed coatings usually incorporate process-dependent defects such as globular pores, interlamellar pores, cracks (in case of ceramics), etc. Porosity is a prevalent feature in the microstructure and affects various coating properties such as elastic modulus, thermal conductivity and dielectric behaviour. This study is conducted to improve the image analysis (IA) as a reliable method for characterization of porosity in thermally sprayed coatings. The versatility of IA methods for microstructural quantification has been investigated for TBCs deposited with partially stabilized zirconia (PSZ), alumina and zirconia–alumina composite coatings by gas tunnel type plasma spraying. This study confirms the applicability of image analysis as a straightforward, versatile, reliable and inexpensive method for porosity analysis agreed with coating qualities and the influences of the Vickers hardness. The paper also discusses the thermal behaviour and high temperature oxidation resistance of the $Al_2O_3$ coatings as compared to composite coatings at the interface. This interlayer is preferred to minimize the detrimental effect of phase transformation of $\gamma$-$Al_2O_3$ to $\alpha$-$Al_2O_3$.


*Keywords:* Plasma deposition; Zirconia–alumina composite coatings; Hardness; Porosity; Image analysis; Oxidation

## 1. Introduction

Plasma sprayed zirconia coatings are widely used as thermal barrier coatings (TBC) in gas turbine hot section components such as burners, transition ducts, vanes and blades. However, their use in diesel engine combustion chamber components has been quite rare, because of the long run durability problems in such conditions. For that reason, there have been many investigations in developing proper TBCs for diesel engines [1,2].

Normally the increased thickness of TBCs leads to a reduced coating lifetime. We can say that the thicker the coating, the higher the temperature gradient through the coating, the higher the stresses in the coating. The coefficient of thermal expansion (CTE) difference of the substrate and coating induces stresses at high temperatures at the coating interface. The strain tolerance of thick TBCs has to be managed by controlling the coating microstructure. Use of thicker coatings generally leads to the higher coating surface temperatures that can be detrimental, if a certain limit is exceeded. In the long run, the phase structure of yttria stabilized zirconia $8\%Y_2O_3$–$92\%ZrO_2$ is not stable above the 1250 °C and can be unstabilized quite fast at 1400 °C [3,4].

Lots of studies have been related to reducing young's modulus and residual stresses of thick TBCs [5]. In practice these can be achieved by controlling the spray parameters, as well as controlling the substrate and coating temperature during the coating deposition. Spray parameters can also be fixed to obtain desired level of porosity and microcracks. Extremely high porosity values (upto 25 vol.%) of TBC s have been obtained by spraying polymers together with zirconia.

Now, the gas tunnel type plasma spraying developed by the author [6] has superior property as compared to the conventional type plasma spray method. A high hardness ceramic coating could be obtained by means of the gas tunnel type plasma spraying, which was investigated in the previous study in detail [7–13]. Usually the Vickers hardness of this sprayed coating became 20–30% higher than that of conventional plasma spraying. Zirconia composite coating formed by gas tunnel type plasma spraying has a high hardness layer at the surface side of the coating, which shows the graded functionality of hardness [14,15]. With the increase in the traverse number of plasma spraying, the hardness distribution was much smoother, corresponding to the result that the coating became denser. The combination of high

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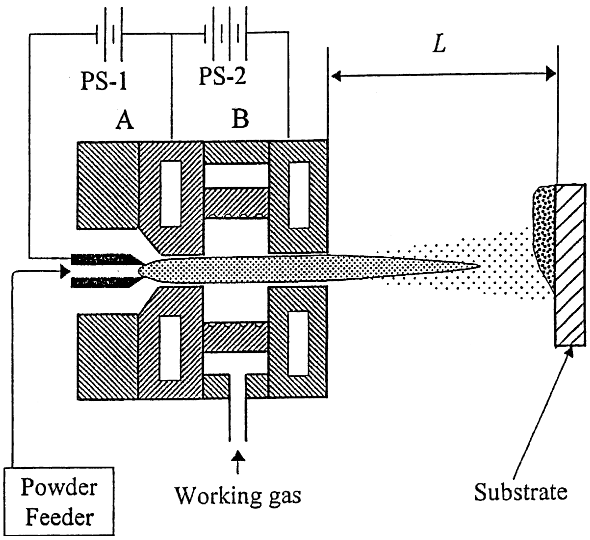


Fig. 1. Schematic of the gas tunnel type plasma spraying torch system.

hardness of $Al_2O_3$ with the low thermal conductivity of $ZrO_2$ will contribute to the development of high functionality graded TBC with higher wear resistance [16].

Microstructural characterization of thermal spray coatings involves quantitative measurements of geometrical features such as porosity (in the form of voids, cracks and other defects) and analysis of material aspects in the coatings such as splat structure, interfaces, phases, etc. Various methods are employed for quantitative measurement of porosity, which forms an important and integral part of microstructural characterization of thermal spray coatings. Many studies have been conducted to establish image analysis as a reliable method for characterization of porosity in thermal spray coatings [17,18].

In this study the microstructures of 8%$Y_2O_3$–92%$ZrO_2$, 100% $Al_2O_3$ coatings and composite coatings 20%$ZrO_2$–80%$Al_2O_3$, 50%$ZrO_2$–50%$Al_2O_3$, 80%$ZrO_2$–20%$Al_2O_3$ TBCs were characterized. The feasibility of producing functionally graded plasma sprayed coatings of $ZrO_2/Al_2O_3$ were explored. The physical, mechanical and thermal properties and high temperature oxidation behaviour of the as sprayed functionally graded TBCs were determined and analyzed in the context of studying the effectiveness of $Al_2O_3$ layer functioning as an oxidation barrier.

## 2. Experimental procedure

Fig. 1 shows the gas tunnel type plasma spraying torch used in this study. The experimental method to produce the high hardness ceramic coatings by means of the gas tunnel type plasma spraying have been described in the previous papers [7–13]. The spraying powder is fed inside plasma flame in axial direction from center electrode of plasma gun. The coating was formed on the substrate traversed at the spraying distance: $L$. The square plates SUS304 were previously sandblasted and cleaned in acetone. The substrate dimensions were 50 mm × 50 mm × 3 mm. In this case, the gas divertor nozzle diameter was $d = 20$ mm. Deposition conditions are presented in Table 1.

The power input to the plasma torch was about $P = 21$ kW, and the power input to the pilot plasma torch was turned off which was supplied by the power supply PS-1, after starting of the gas tunnel type plasma jet. The spraying distance was short distance of $L = 40$ mm.

Table 1
Experimental conditions

| | |
|---|---|
| Powder | $ZrO_2$, $Al_2O_3$ and $ZrO_2/Al_2O_3$ mixture |
| Traverse number, $N$ | 2 and 4 |
| Power input, $P$ (kW) | 17–21 |
| Working gas flow rate, $Q$ (l min$^{-1}$) | 180 |
| Powder feed gas, $Q_{feed}$ (l min$^{-1}$) | 10 |
| Spraying distance, $L$ (mm) | 40 |
| Traverse speed, $v$ (cm min$^{-1}$) | 50 and 100 |
| Powder feed rate, $w$ (g min$^{-1}$) | 25–45 |
| Gas divertor nozzle dia., $d$ (mm) | 20 |

The working gas was Argon with flow rate of $Q = 180$ l min$^{-1}$, and the gas flow rate of carrier gas was 10 l min$^{-1}$. The powder feed rate of zirconia–alumina mixed powder was $w = 25 - 45$ g min$^{-1}$. The traverse speed of the substrate was changed the value from $v = 50 - 100$ cm min$^{-1}$. Also the number of traverse was changed two to four times. The thickness of the coating was 140–250 μm.

The chemical composition and the particle size of zirconia and alumina powders are shown in Table 2. The zirconia powder was commercially prepared type of K-90 (YSZ of 8%$Y_2O_3$) and alumina powder was the type of K-16T. The mixing ratio of alumina to zirconia powders are varied from 20 to 80 wt%.

The Vickers hardness was measured with a high quality digital micro hardness tester (MATSUZAWA-MXT50) with 0.5 N load, its load time was 15 s along the whole cross section. It was calculated as 10 points measurements. The distribution of the Vickers hardness in the cross section of the zirconia composite coating was measured at each distance from the coating surface in the thickness direction.

The morphology of the coatings was analyzed by optical microscope (NIKON, Japan). Micrographs with two magnifications (200× and 400×) from polished cross sections were used for image analysis for the determination of the total porosity and the porosity profile through the cross-section.

To evaluate the effectiveness of alumina interlayer on the oxidation resistance of plasma sprayed TBC samples were heat treated in ambient environment at 1050 °C for 5 h allowing the oxide scale to grow at the substrate–topcoat interface. The same oxidation test was also performed on free standing coatings. Microstructural characterizations using SEM (NIKON-ESEM 2700) equipped with and energy dispersive X-ray spectrometry (EDS) were conducted on the as sprayed and heat treated samples to examine any change in microstructure and chemical composition of coatings. X ray diffraction (JEOL JDX-3530M) analysis was also performed to characterize material phases before and after heat treatment.

## 3. Results and discussion

### 3.1. Microstructural characterization

The optical cross sectional micrographs of zirconia composite coatings are shown in Fig. 2. The figure shows the microstructure of the pure zirconia (Fig. 2a), pure alumina (Fig. 2b) and composite coatings (Fig. 2c). The thickness of all coatings and the distribution of porosity along the cross section were measured by image analysis. The coatings present a

Table 2
Chemical composition and size of zirconia and alumina powder used

| | Composition (wt.%) | | | | | Size (μm) |
|---|---|---|---|---|---|---|
| $ZrO_2$ | $ZrO_2$ 91.65 | $Y_2O_3$ 7.72 | $Al_2O_3$ 0.02 | $SiO_2$ 0.01 | $Fe_2O_3$ 0.14 | 10–45 |
| $Al_2O_3$ | $Al_2O_3$ 99.8 | $Na_2O$ 0.14 | $SiO_2$ 0.01 | $Fe_2O_3$ 0.01 | | 10–45 |