

# Laser surface treatment of plasma-sprayed yttria-stabilized zirconia coatings

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## Abstract

A continuous wave CO<sub>2</sub> laser with a defocused beam has been employed to seal the surface layer of plasma-sprayed of 8wt. % yttria-stabilised zirconia coatings on AISI 1045 steel substrate. The effect of laser remelting on microstructure and corrosion resistance of plasma-sprayed layer was investigated. The microstructure of the sealed layer presented a cellular structure which grows perpendicular to the surface. The micrographs have shown small cracks and absence of porosity. The corrosion resistance was analysed by the EIS and polarisation tests by using a 3 % NaCl solution. Laser sealing improved the corrosion resistance of the coating and increased the microhardness.

## Keywords

Laser surface treatment. Yttria-stabilised zirconia. Plasma-sprayed. Corrosion resistance.

## Tratamiento superficial por láser de recubrimientos por proyección por plasma de ZrO<sub>2</sub> 8 % Y<sub>2</sub>O<sub>3</sub>

## Resumen

Un equipo láser continuo de CO<sub>2</sub>, con potencia nominal de 1 kW, se utilizó para sellar la superficie revestida con ZrO<sub>2</sub> 8 % Y<sub>2</sub>O<sub>3</sub> por proyección por plasma sobre un sustrato de acero AISI 1045. Se investigaron los efectos del tratamiento de fusión con láser sobre la microestructura y la resistencia a la corrosión del recubrimiento. La resistencia a la corrosión se analizó por medidas electroquímicas en una solución de NaCl al 3 %. Las micrografías mostraron que la superficie del revestimiento presentó varias grietas pequeñas, sin embargo, no fueron observados poros. La microestructura de la capa sellada presentó una estructura en forma de columnas con crecimiento perpendicular a la superficie libre. El sellado a láser mejora la resistencia a la corrosión de los recubrimientos y aumenta la microdureza.

## Palabras clave

Tratamiento superficial por láser. Zirconia estabilizada con ítrio. Proyección por plasma. Resistencia a la corrosión.

## 1. INTRODUCTION

Zirconia ceramics present a combination of high chemical stability, high wear resistance, high toughness, low thermal conductivity, that make this group of materials particularly attractive for applications in harsh environments under severe loading<sup>[1-6]</sup>.

Plasma spray process is widely used in the application of zirconia ceramics coatings. However, these coatings typically contain porosity that permit contaminants to penetrate through the coating attacking the substrate. In addition, porosity and cracks can lead to degradation, destabilisation, spalling and loss of thermal

insulation and corrosion protection of the plasma-sprayed coatings<sup>[7-14]</sup>.

Laser surface melting is a promising process for improving the performance of the plasma-sprayed coatings by reducing porosities, densifying the coating, reducing surface roughness and improving its protective efficiency<sup>[15-18]</sup>. Fine microstructures, resulting from rapid cooling from the melt, together with smooth and shiny layers are characteristic features of the laser sealing<sup>[14]</sup>. The plasma-sprayed zirconia coatings sealed by laser have been the subject of several investigations<sup>[7-10 and 12-27]</sup>. These studies have shown that the sealed coatings present a better performance as to cavitation erosion resistance<sup>[25]</sup>,

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surface spalling when they were subjected to a high heat flux environment<sup>[26]</sup>, and lifetime<sup>[27]</sup> compared with those as-sprayed coatings.

The purpose of this study is to investigate the influence of laser sealing process on hardness and corrosion resistance of surface coatings of ZrO<sub>2</sub> 8wt. % Y<sub>2</sub>O<sub>3</sub> produced by plasma spray.

## 2. MATERIALS AND EXPERIMENTAL PROCEDURE

Zirconia coatings were prepared by atmospheric plasma spraying of 8wt. % yttria-stabilised zirconia powder on an AISI 1045 steel substrate (65 × 12 × 6 mm<sup>3</sup>) by using a plasma gun 3MBII SULZER METCO. The samples were first grit blasted with alumina powder. No bond layer was applied on the substrate. The thickness of the coating was about 200 µm.

A 1 kW continuous wave CO<sub>2</sub> laser with TEM<sub>00</sub> defocused beam was used to seal the surface layer of the plasma-sprayed coating. Argon was used as a protective gas. In order to cover completely the surface of the coating, the samples were subjected to multiple scans, with an overlap of 20 % between consecutive tracks, always in the same direction. The plasma-spraying and laser sealing conditions are given in table I.

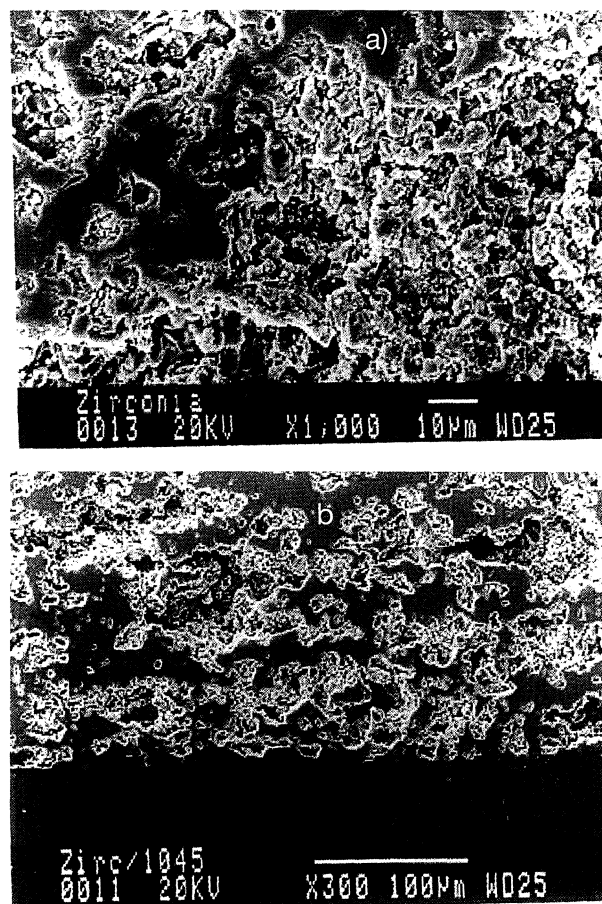
The coatings microstructures were characterised by optical microscopy, scanning electron microscopy and X-ray diffraction. Microhardness measurements were carried out on the transverse section with a load of 100 gf for both as-sprayed and as-sealed layer conditions. Roughness measurements "Ra" were carried out using a SJ-201 MITUTOYO Surface Roughness Tester.

The corrosion behaviour of the coatings was analysed under aggressive 3 % NaCl solutions at room temperature. The electrochemical impedance

spectroscopy (EIS) and the polarisation tests were carried out using a Potentiostat/Galvanoplast Model 273A coupled to a SOLARTRON 1250 Frequency Response Analyser, a glass corrosion cell kit with the working electrodes, a plate platinum counter-electrode and saturated calomel reference electrode (SCE). The polarisation tests were conducted in a scan rate of 0.2 mVs<sup>-1</sup> from -250 mV/SCE to + 250 mV/SCE in a open-circuit potential.

## 3. RESULTS AND DISCUSSION

The coatings produced by plasma spraying presented a thickness of about 200 µm. Figure 1 shows a top view (a) and the transverse section (b) of the as-sprayed coating which exhibited high porosity, approximately 10 % in area, as well as vertical and horizontal microcracks. The surface roughness of the coatings was about Ra = 10 µm and the average microhardness about 900 HV.



**Figure 1.** Typical top view of the as-sprayed coating (a) and transverse section (b).

*Figura 1. Aspecto de la superficie (a) y de la sección transversal (b) de la capa de ZrO<sub>2</sub> 8wt. % Y<sub>2</sub>O<sub>3</sub> depositada por proyección por plasma.*

**Table I.** Plasma spraying and laser sealing parameters

*Tabla I. Parámetros de la proyección por plasma y sellado a láser*

Plasma spraying Parameters		Laser sealing Parameters	
Voltage (V)	70	Power (kW)	0.8 – 1.0
Current (A)	450	Beam diameter (mm)	3.5 – 5.0
Arc gas pri. – Ar(l/min)	80	Scanning speed (mm/s)	33.3 – 300
Arc gas sec. – H <sub>2</sub> (l/min)	15	Power density (W/mm <sup>2</sup> )	40.7 – 103.9
Carrier gas – Ar(l/min)	30		
Spray distance (mm)	120		

This value is about 38 % higher than that reported for Mohammed-Jasim *et al.*<sup>[13]</sup> for the same coating composition.

The diffraction patterns for both starting powder and the as-sprayed coating are shown in figure 2 and present mainly cubic (c) and tetragonal (t) phases. The monoclinic phase which is present in the starting powder has also been detected in the as-sprayed layer.

To produce the sealed coatings several experiments were carried out, under various combinations of the laser operating parameters (Table I), in order to determine the best conditions for laser sealing. The tests were necessary since available data in the literature are still incomplete and even contradictory. The experiments have shown that the depth of the sealed layer increases with increasing power and with decreasing scan speed. Numerous depressions, attributed to gas evolution, were observed on the sealed surface. The average size and the amount of depressions decrease with increasing scan speed, but increase with increasing power. Similar observations have been reported in the literature<sup>[14 and 28]</sup>

From the tests, three coatings, namely S1, S2 and S3, presented the best results in terms of porosity, cracks, roughness and depth sealed. They were produced by using the following parameters: Power: 1000W, Laser beam diameter: 5mm, Scan speed: S1: 200 mm/s, S2: 300 mm/s, S3: 350 mm/s. The diffraction patterns for these coatings are shown in figure 3. All the coatings have microstructures consisting of: cubic (c), tetragonal (t) and non-transformable tetragonal (t') phases.

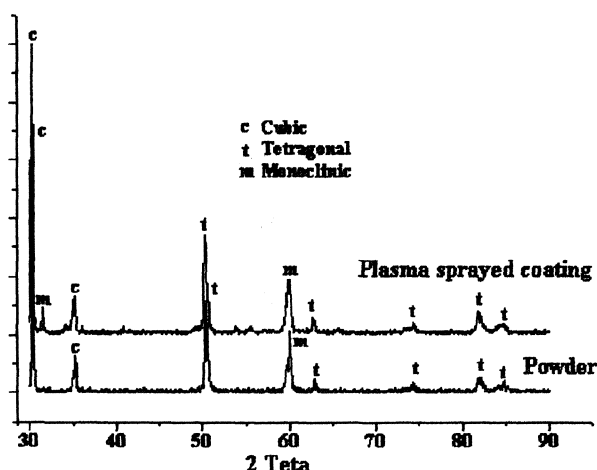


Figure 2. XRD patterns for starting powder and as-sprayed layer.

Figura 2. Difractogramas de polvo y de la capa depositada por proyección por plasma.

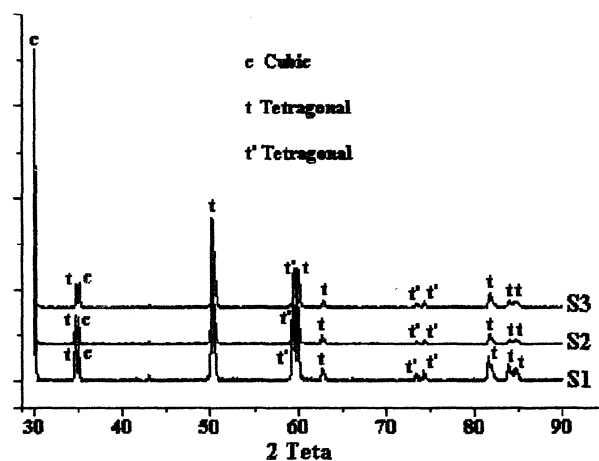


Figure 3. XRD patterns for S1, S2 and S3 coatings.

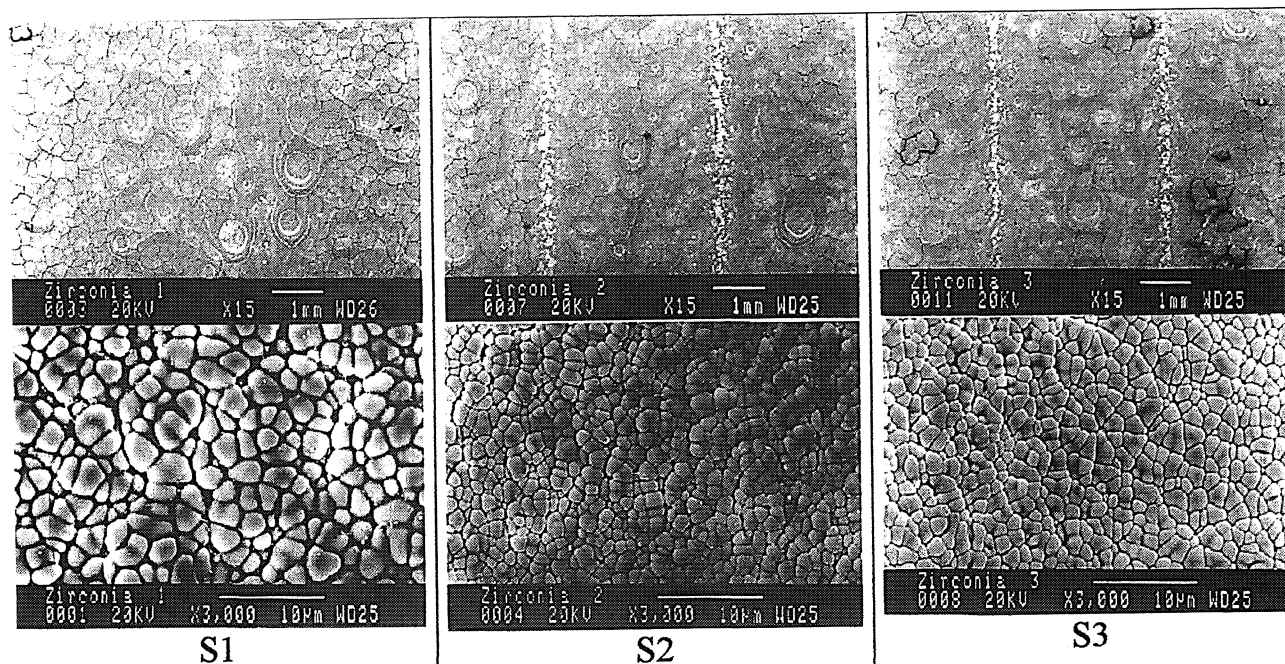
Figura 3. Difractogramas de las capas S1, S2 y S3.

No monoclinic phase was detected. The rapid cooling rate have induced the production of non-transformable tetragonal t' phase during solidification.

The typical micrographs of S1, S2 and S3 coatings are shown in figure 4. It can be seen that, the coatings presented a cellular structure. The cell size decreased with increased scan speed. The structure of the S3 coating was the same of S2 coating but with a higher amount of cracks. The S2 coating presented the best characteristics when compared with S1 and S3 coatings.

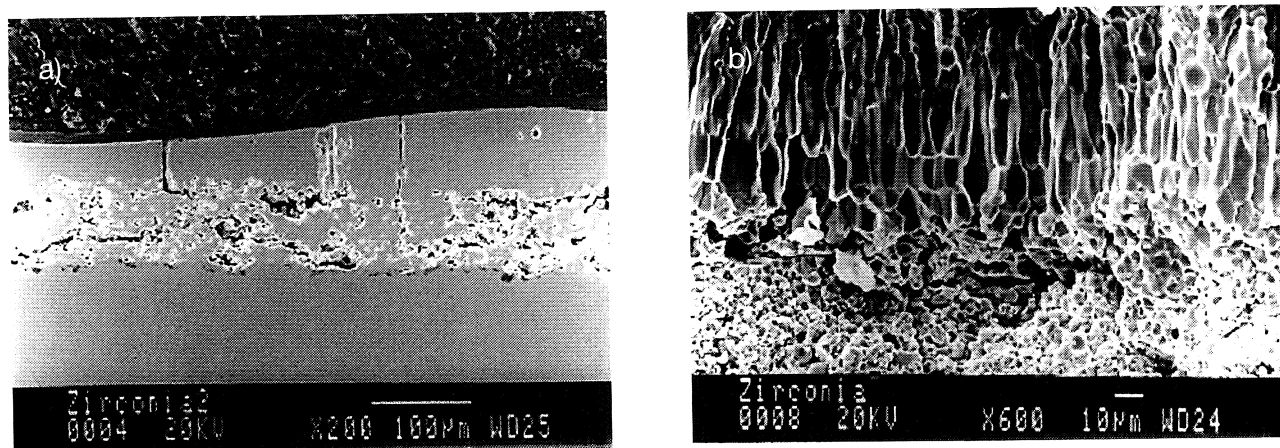
The analysis of the S2 coating has shown a dense resolidified layer (absence of porosity) with a homogeneous fine cellular structure. The sealed surface was smooth, shiny and segmented (network of cracks). The depth of the sealed layer was about 95  $\mu\text{m}$  and the surface roughness was about  $R_a = 3.6 \mu\text{m}$ . The microhardness, measured on the transverse section of the S2 coating, was about 1700 HV which is significantly higher than that observed at the as-sprayed coating condition (900 HV). The microstructure of the transverse section of the sealed layer was revealed by fracturing the coating (Fig. 5). It consists of a cellular structure that grows perpendicularly to the free surface. The dendritic structure, as described by Shied and Wu<sup>[29]</sup>, was not detected in the present experimental investigation.

A comparative study of corrosion behaviour of the as-sprayed and as-sealed coatings is shown in figure 6. As expected, the corrosion behaviour of these coatings is strongly dependent on the treatment conditions. For all coatings experimentally examined, both types of corrosion



**Figure 4.** Typical SEM micrographs of the S1 (a), S2 (b) and S3 (c) coatings.

*Figura 4. Aspecto de las micrografías MEB de las capas S1 (a), S2 (b) y S3 (c).*



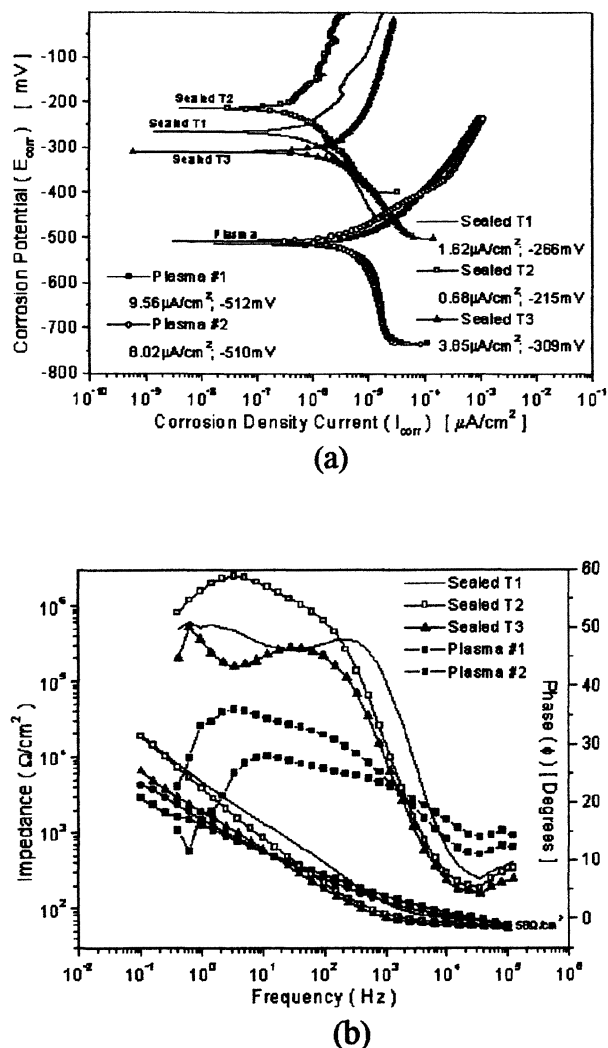
**Figure 5.** SEM of the transverse section of the S2 coating.

*Figura 5. MEB de la sección transversal de la capa S2.*

tests have shown similar results in terms of corrosion behaviour. It can also be observed that the three sealed coatings presented better corrosion resistances when compared with as-sprayed coatings.

The sealed coatings have shown a higher susceptibility to improve corrosion resistance due to absence of porosity. They exhibited a range of corrosion rates from 0.68 to 3.85  $\mu\text{A}/\text{cm}^2$  and as-sprayed coating a range between 8.02 to 9.56  $\mu\text{A}/\text{cm}^2$ . In addition, the corrosion potential has shown a significant difference about

200 mV toward the noble side. It can also be observed in figure 6a) a difference in corrosion behaviour between the three sealed coatings. The micrographs shown in figure 4, permit to observe a strong influence of the microstructure on the corrosion resistance. The best corrosion resistance was obtained for the S2 sealed coating, which has presented a denser and fine cellular structure. This structure has presented better results in terms of homogeneity, grain size and crack incidence than the other two sealed coatings.



**Figure 6.** Polarization curves (a) and EIS diagrams (b), respectively, of the as-sprayed and as-sealed coatings in a 3 % NaCl solution.

Figura 6. Curvas de polarización (a) y Diagramas EIS (b) de las capas de proyección por plasma y selladas por láser en una solución NaCl al 3 %.

## 5. CONCLUSIONS

Plasma sprayed  $ZrO_2$  8wt. %  $Y_2O_3$  coatings have been laser sealed under different operating parameters and the characteristics of the sealed layer were analysed. The following conclusions can be drawn:

- A shiny surface layer of low roughness and fine cellular structure on the plasma sprayed zirconia coatings was produced by laser sealing process.
- The sealed layer presents a network of cracks which are perpendicular to the free surface but is free of porosity.

- The structure of the sealed layer is cellular and grows perpendicular to the free surface of the coating.
- The sealed layer consists of cubic, tetragonal and non-transformable tetragonal phases. No monoclinic phase was observed in any case experimentally examined.
- Laser sealing increases the microhardness from about 900 HV for an as-sprayed layer to about 1700 HV for the as-sealed layer.
- The sealed coatings have shown better corrosion resistance than the as sprayed coatings due to the absence of porosity.
- The corrosion behaviour is strongly dependent on the treatment conditions.
- Both EIS and polarisation tests have shown similarity in terms of corrosion behaviour for as-sprayed and as-sealed coatings performed in a 3 % NaCl solution.

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