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CHARACTERIZATION OF AS-SPRAYED AND LASER-TREATED ZIRCONIA-BASED PLASMA SPRAYED COATINGS

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Résumé: On examine les propriétés de revêtements de zircone bruts et traités laser. Les compositions chimiques, structures cristallines, durées, résistances au cyclage thermique sont comparées et commentées.

Abstract: The properties of both basic zirconia-based and laser-treated layers are examined. Chemical compositions, crystal structures, hardnesses, and thermal cycling behaviours are compared and discussed.

The temperature range reached in diesel engines or gas turbines has led the industrial designers to protect the metallic parts with insulating coatings. Partially stabilized zirconia (PSZ) plasma spraying is a classical technics. Predeposited superalloys NiCrAlY as bond layers improve the adhesion of the coatings /1,2/.

We study a 3-layers atmospheric plasma-sprayed coating: 2 NiCrAlY bond-coats and 1 ZrO₂-Y₂O₃ PSZ. This coating is then treated with a scanning powerful laser, which melts instantaneously the layers. This treatment is supposed to improve some properties of the coating: cycling resistance, adhesion, hardness, compacity.

Our study consists in comparing the properties of both as-sprayed and laser-treated coatings, from macroscopic and microscopic points of view. This research is part of a collaboration program between Baikov Institute of Metallurgy, where coatings and laser treatments are realized, and IMP, where coatings are characterized.

1: COATING AND LASER TREATMENT

Coating

The surface of the substrate (refractory stainless steel) is grit blasted with alumina. The plasma-producing gas is a mixture Ar + H₂. The particles are blown-in with an Ar flow perpendicular to the torch axis (F4 HB type). The 3 layers are successively deposited. The main parameters of the plasma-spray are given in the following table:

<table>
<thead>
<tr>
<th>layer</th>
<th>target distance</th>
<th>particles size</th>
<th>Ar flow-rate</th>
<th>H₂ flow-rate</th>
<th>plasma torch power</th>
</tr>
</thead>
<tbody>
<tr>
<td>down NiCrAlY</td>
<td>135 mm</td>
<td>50-80 μm</td>
<td>42 1/min</td>
<td>6 1/min</td>
<td>--</td>
</tr>
<tr>
<td>medium NiCrAlY</td>
<td>120 mm</td>
<td>100-150 μm</td>
<td>42 1/min</td>
<td>8 1/min</td>
<td>40 KW</td>
</tr>
<tr>
<td>+ 30% ZrO₂-Y₂O₃ (stab.: 6-8% Y₂O₃)</td>
<td>120 mm</td>
<td>150-200 μm</td>
<td>42 1/min</td>
<td>8 1/min</td>
<td>40 KW</td>
</tr>
</tbody>
</table>

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Laser treatment

Only the surface is concerned. The laser scans the surface linearly at a constant controlled speed. The laser is a CO₂ one. 2 different treatments are used: pulse periodic or continuous action. The main parameters of the laser treatments are given in Fig.1.

<table>
<thead>
<tr>
<th>pulse periodic laser</th>
<th>continuous laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>E=7 J</td>
<td>P: 550 W 850 W 1500 W 2000 W 2000 W 2500 W</td>
</tr>
<tr>
<td>φ=1.2 mm</td>
<td>v: 40 mm/s 40 mm/s 11 mm/s 11 mm/s 18 mm/s 11 mm/s</td>
</tr>
<tr>
<td>τ=4 ms</td>
<td></td>
</tr>
<tr>
<td>v=2 Hz</td>
<td></td>
</tr>
<tr>
<td>v=1 and 1.5 mm/s</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1: laser treatment description

2: COATINGS EXAMINATIONS AND ANALYSIS

2-1: Surface macroscopic aspect

as-sprayed coating  pulse periodic laser-treated  continuous laser-treated

rough light grey 
light grey dull

splintery black bright
bright blistered dark grey

The dark color of the laser-treated surfaces could be connected with a stoechiometric deviation, or from metallic components migration, as it is suggested by the bright aspect of the surface.
2-2: Microscopic cross-section view (EEM images)

Figure 2: cross-section views of as-sprayed coating
Figure 3: cross-section views of laser-treated coating
Figure 4: cross-section views of laser-treated coating
The as-sprayed coating structure is uniform. After laser treatment, it becomes irregular, as it is suggested by Fig.1. The substrate/superalloy interface contents in both cases wide pores (≥10μm): a weak adhesion is expected. The superalloy NiCrAlY (60 μm in thickness) and the NiCrAlY + ZrO₂-Y₂O₃ layer (40 μm in thickness) present a high porosity in the as-sprayed coating, with micropores and long pores (see Fig.2). After laser treatment, these bond-coats do not subsist everywhere. Fluid aspect remains, but with wider homogeneously colored areas. Microporosity still subsists, with darker areas near the pores. We notice large homogeneous areas (a few 10μm i.d.) in the upper part of the coating. The as-sprayed zirconia layer, 30 to 50 μm in thickness, has a crushed droplets feature (length>200 μm), with microcracks and micropores (see Fig.2). The laser-treated zirconia structure is made of flat stacked tiles (2 to 20μm in thickness, 15 to 200μm in length). Microporosity has disappeared, but wide cracks (5 μm) remain between the tiles (see Fig.3 & 4).

2-3: Chemical composition, elements localization

The results of microprobe analysis are presented Fig.5 & 6: detected X rays response of Zr, Ni, Cr, Al, Fe, along a cross-section of the coating.

![Figure 5: composition analysis of as-sprayed coating cross-section](image1)

![Figure 6: composition analysis of laser-treated coating cross-section](image2)
After laser treatment, components of superalloy are separated (see Fig.6). Al concentrates around the pores, in dark areas shown on the EEM images (see Fig.3 & 4). Ni and Cr gather inside bulks. Al and Cr scatter to zirconia; that could give a dark color to the laser-treated coating.

The quantization of every elements (and of their oxides) is necessary to analyse the chemical reactions that occur in the coating during laser treatment.

2-4: Crystal structure of yttried zirconia

Fast cooling conditions after plasma spraying, and the $Y_2O_3$ rate in the yttried zirconia, are the major parameters that influence the crystal structure of the system at room temperature /4/. The quench of yttried zirconia drops could produce a metastable tetragonal phase, with lower $Y_2O_3$ rate than the stable phase, and strongly connected to the mechanical behaviour of the coating /2,5/.

The crystal structure of as-sprayed zirconia coating on the substrate has been analysed with X-diffractometer. Only cubic peaks have been detected (see Fig.7). Different causes could explain this result: (1) Distortions from microstresses could hide the tetragonality /6/ (2) $Y_2O_3$ rate (6 to 8%) and quench speed could stop the cubic $\rightarrow$ tetragonal phase transformation (3) Straight cubic $\rightarrow$ metastable tetragonal phase transformation occurs /7/, but tetragonality (ie: c/a rate) remains too low to let corresponding peaks appear on the diffraction spectrum.

![X diffraction spectrum of as-sprayed and laser-treated surfaces](image_url)

Figure 7: X diffraction spectrum of as-sprayed and laser-treated surfaces

The modifications of crystal structure of PSZ during annealing have been described in the litterature /8,9/. Laser treatment has a different effect: the melting of a great area (>1 mm, 100 μm in deepness for the most powerful). The cooling rate is slower than the quench speed after plasma spray, because of the greater heat capacity effect of the melted material.

MEB pictures of laser-treated samples (see Fig.3 & 4) show a specific grain organization inside the zirconia tiles: the orientation of this "fishbone" structure follows the temperature gradient lines. This organization is sometimes attributed to a rhombohedric crystal structure. The modification of the mesh size would be very tiny in this case, since only cubic diffraction peaks are detected (see Fig.7).
Decreasing of diffraction peaks width is noticed after laser treatment. This result could be explained first by an increasing of the crystal size, and then by a more homogeneous distribution of the interplanar distances. This last assumption suggests that the residual microstresses are greater after plasma spray than after laser treatment. Cooling and solidification occur without mechanical effect in this last case (natural convection in the liquid phase does not produce any perturbation).

2-5: Zirconia layer microhardness

Measurements have been made with a Vickers microhardness equipment, on cross-sections of as-sprayed and laser-treated coatings, under a 25g load. Zirconia hardness is multiplied by 2.3 after laser treatment (see table below).

<table>
<thead>
<tr>
<th>VICKERS HARDNESS</th>
<th>As-sprayed coating</th>
<th>Pulse periodic laser-treated</th>
<th>Continuous laser-treated coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>average of 5 results</td>
<td>920 ±100</td>
<td>2020 ± 200</td>
<td>2140 ± 200</td>
</tr>
</tbody>
</table>

Laser-treated zirconia appears more brittle: tiles fail under a 50g load. As-sprayed zirconia, which is already microcracked, seems to be tougher.

2-6: Temperature cycling resistance

The classical ageing process is annealing /10,11/. In our case, the coating is submitted to a slow and large range temperature cycling, in order to produce structure modifications and stresses that could lead to the layer destruction. Heating and cooling rates are +2°C/s and -1°C/s, between room temperature and 1150°C. Both as-sprayed and laser-treated samples are tested with the following process: concentrated and modulated solar radiant heat is applied on the substrate side. The coating surface temperature is measured by a radiant signal detection and quantization system using an optic fiber coupled with a 2-color pyrometer /12/.

As-sprayed coating.

1150°C

- cracks on the surface
- duration: 3mm

50°C

- spalling
- scales 0.5mm
- duration: 30min

150°C

- scales >1mm
- duration: 20min

400°C
Destruction processes only appear during the cooling steps, but temperature thresholds increase during ageing. All destruction process intensities have the same time-dependance shape: maximum intensity at the 2/3 of the process duration.

**Pulse periodic laser-treated coating**

1150°C

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Color/Aspect</th>
<th>Spall Type</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>Grey, Vitreous</td>
<td>1st Spall</td>
<td>Min 3min</td>
</tr>
<tr>
<td>80°C</td>
<td>Brown</td>
<td>Smooth</td>
<td>15min</td>
</tr>
<tr>
<td>400°C</td>
<td>Green</td>
<td>Destruction</td>
<td>15min</td>
</tr>
</tbody>
</table>

The destruction process is quicker, but it occurs later than in the previous case of as-sprayed coating.

**Continuous laser-treated coating**: surface destruction occurs after 2 cycles. The steel substrate has probably been reached by the powerful laser beam (2 kW) during the laser treatment and the substrate/superalloy interface has suffered from the laser action.

The poor cycling resistance of our samples can be explained by the steel substrate and the superalloy oxidation, which is not prevented by the zirconia layer. As-sprayed layer is porous and laser-treated layer is cracked. At high temperature, severe oxidation facilitates delamination of deposited layers. Repeated thermomechanical stresses during cooling periods make these layers break after a short time. It is already proved that the resistance of coatings increases with thickness /1,13/, and that the sprayed particles size is partly responsible for the coating mechanical behaviour /6/.

Mechanical stresses measurements and cycled coatings chemical composition analysis are now necessary to take more advantage of these results.

**3: CONCLUSION**

The effect of laser treatment on an yttried zirconia plasma-sprayed coating has been studied, through the analysis of a few properties. Hardness is improved, with lower toughness. Thermal cycling resistance improvement was not demonstrated. Bond-coat oxidation does not seem to be prevented after the laser treatment.

Microscopic observations have shown great modifications of zirconia layer: a stacked tiles structure was noticed to replace the initial crushed drops organization. Micropores were closed, but cracks appeared. Bond layers locally moved to the surface by convection in the liquid phase during the laser action.

Elements microprobe analysis has shown metallic scattering (Al, Cr) into zirconia, and separation of components inside the superalloy (Ni, Cr, & Al).

Only cubic X-diffraction peaks of zirconia have been detected, but other crystal phases could appear, as it is suggested by the "fishbone" structure observed in the laser treated zirconia.
The development of a laser treatment process in order to improve yttrium zirconia coatings properties needs first the control of plasma-spraying parameters. Further studies of both macroscopic and microscopic properties of as-sprayed and laser-treated coatings, as well as chemical composition, porosity, and adhesion analysis, are necessary to complete our preliminary study. From a theoretical point of view, knowledge models are necessary to describe thermal transfers and phases changes that produce physico-chemical modifications under laser action.

A flash treatment on this kind of coatings, using concentrated solar energy, is under consideration. An action between classic annealing and laser melting should be thus obtained.

REFERENCES


