Hot corrosion behavior of Al2O3 laser clad plasma sprayed YSZ thermal barrier coatings

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Abstract

In the present study, the laser cladding of Al2O3 on the top surface of air plasma sprayed (APSed) yttria stabilized zirconia (YSZ) coatings was carried out to improve the hot corrosion resistance of the thermal barrier coatings (TBCs) in the presence of molten salts. The coatings with and without laser cladding were subjected to a hot corrosion test at 1000 °C for 30 h in which a mixture of 55 wt% V2O5 and 45 wt% Na2SO4 was used as the corrosive salt. SEM micrographs and EDS analysis confirmed the formation of YVO4 rod-shaped crystals dispersed on the surface of the APSed YSZ coatings after hot corrosion test, while these crystals were hardly detected in the laser clad coatings. The SEM micrograph of the cross section of the APSed YSZ coatings revealed cracks and a thermally grown oxide (TGO) layer in the bond coat/top coat interface, which led to the complete delamination of the coatings. Supporting the SEM micrographs, XRD patterns indicated the transformation of metastable tetragonal zirconia (t′-ZrO2) to monoclinic zirconia (m-ZrO2) after hot corrosion test. This structural transformation was due to the reaction of the molten salts with Y2O3 (zirconia stabilizer) which destabilized the t′-ZrO2. To compare the hot corrosion resistance of the APSed YSZ and the laser clad coating, the volume percentage of the undesirable m-ZrO2 was then calculated after the hot corrosion test. This calculation revealed a higher amount of m-ZrO2 in YSZ (about 70 vol%) compared to that of the laser clad coating (about 13 vol%).

1. Introduction

Thermal-barrier coatings (TBCs) are advanced refractory oxide ceramic coatings applied to the surfaces of metallic components of gas-turbine engines, enabling them to operate at higher temperatures [1–4]. As an insulator, TBCs reduce oxidation and thermal fatigue. They also increase the lifespan and the operating temperature and consequently improve the efficiency of gas turbines. Due to the mentioned points, TBCs have been the focus of significant research and development efforts during the last decade and there were a great attempt to develop new and advanced TBCs [5–8].

TBCs typically consist of two layers: a metallic bond coat and a ceramic top coat [1,3,8]. The former is mostly made of NiCrAlY or NiCoCrAlY alloys, which are more oxidation resistant than the substrate and play a key role in the improvement of adhesion of the metallic substrate to the ceramic top coat [9,10]. Among all materials used as ceramic topcoat, yttria-stabilized zirconia (YSZ) has attracted more attention due to its unique properties such as low thermal conductivity, high melting temperature and high coefficient of thermal expansion [7,11]. A thermally grown oxide (TGO) layer also forms during the service at elevated temperatures between the bond coat and the top coat and acts as an oxygen diffusion barrier [6,12].

Despite the advantages, YSZ provides poor hot corrosion resistance, especially in an atmosphere consisting of vanadium, sodium and sulfur, as in the case of impure fuels used in industrial gas turbines [13–16]. During combustion in the gas turbine at elevated temperatures, sodium sulfate (Na2SO4) forms as a result of a chemical reaction between sulfur (from impure fuel) and sodium chloride. Vanadium also reacts with oxygen and produces V2O5. Then Na2SO4 and V2O5 condense on the YSZ layer, react with yttria and lead to the depletion of Y2O3 from YSZ. This depletion destabilizes the metastable tetragonal zirconia (t′-ZrO2) and transforms it to monoclinic zirconia (m-ZrO2). The t′ → m-ZrO2 transformation is introduced as the main factor of delamination and degradation of TBCs [13,15].

To improve the hot corrosion resistance of TBCs, many attempts have been made and different methods have been used by...
researchers. One of the promising approaches is to more stabilize the t′-ZrO₂ via adding more acidic stabilizers such as CeO₂, In₂O₃, Sc₂O₃ and YTaO₄ to YSZ [14,17–19]. Laser glazing is another method which makes TBCs impermeable, by providing a dense and pore-free layer, which reduces molten salt infiltration [20–22]. Ahmadi-Pidani et al. [23] investigated the effect of laser glazing of ceria-yttria stabilizes zirconia (CYSZ) on the hot corrosion resistance of the coating in the presence of Na₂SO₄ and V₂O₅ molten salt. Their results revealed a more than twofold enhancement of hot corrosion resistance. Deposition of an alumina overlay on the surface of the YSZ coating by EB-PVD [24], APS [25] and dip coating method [26] has recently investigated, which improved the hot corrosion and thermal shock resistance of TBCs. Afrasiabi et al. [5] evaluated the hot corrosion behavior of particle and layer composites of Al₂O₃-YSZ applied to the surface of Inconel 738 via plasma spray. Their results indicated minor structural transformation of tetragonal to monoclinic zirconia, which confirm the improvement of hot corrosion resistance of TBCs in contact with Na₂SO₄ and V₂O₅ molten salts.

Although adding alumina to YSZ has been studied before [22,25,26], laser cladding of Alumina on the surface of YSZ has not been investigated. In the present study, due to the excellent corrosion resistance of Al₂O₃ and its very low solubility in molten salts [27], the authors tried to increase the hot corrosion resistance of APSed TBCs via laser cladding of Al₂O₃ (as a protector of YSZ) on the outer surface of YSZ. The hot corrosion behavior of the TBCs in the presence of Na₂SO₄ and V₂O₅ molten salts after laser cladding.

![Image](image1.png)

**Fig. 1.** The FESEM micrographs of (a) the NiCoCrAlY, (b) the conventional YSZ and (c) the Al₂O₃ spray powders.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>NiCoCrAlY</th>
<th>YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (A)</td>
<td>600</td>
<td>500</td>
</tr>
<tr>
<td>Voltage (V)</td>
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<td>80</td>
</tr>
<tr>
<td>Primary gas, Ar (SLPM)</td>
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<td>35</td>
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<tr>
<td>Secondary gas, H₂ (SLPM)</td>
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<td>12</td>
</tr>
<tr>
<td>Carrier gas, Ar (SLPM)</td>
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<td>2.6</td>
</tr>
<tr>
<td>Powder feed rate (g/min)</td>
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<td>20</td>
</tr>
<tr>
<td>Spray distance (mm)</td>
<td>120</td>
<td>120</td>
</tr>
</tbody>
</table>

* Standard liter per minute.

**Table 1**
The plasma spraying parameters.

**Table 2**
The laser cladding parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average power (W)</td>
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</tr>
<tr>
<td>Pulse frequency (Hz)</td>
<td>30</td>
</tr>
<tr>
<td>Scanning speed (mm/s)</td>
<td>5</td>
</tr>
<tr>
<td>Argon flow rate (SLPM)</td>
<td>10</td>
</tr>
<tr>
<td>Powder carried gas flow rate (l/min)</td>
<td>20</td>
</tr>
<tr>
<td>Powder feeding rate (g/min)</td>
<td>0.35</td>
</tr>
</tbody>
</table>

![Image](image2.png)

**Fig. 2.** The SEM micrographs of: (a) the top surface and (b) the cross section of the APSed YSZ.
was then discussed and compared to that of the conventional APSed YSZ.

2. Materials and methods

2.1. Materials

The TBC system, composed of a bond coat (125 ± 25 μm thickness) and a top coat (260 ± 25 μm thickness), was deposited on the INC 738 via APS process using Sulzer Metco AG F4-MB gun. To enhance the adhesion between the TBC coating and the substrate, the surface of INC 738 with the dimension of 2 cm × 2 cm × 1 cm was grit-blasted with alumina particles before APS. The powder used for bond coat was 22SN6883, S.N.M.I. Avignon (Ni-23Cr-18Al-1Y (wt%)) with particle size of 38–75 μm (Fig. 1-a). The ceramic top coat was Sulzer Metco 204 NS trade mark YSZ (7 wt% Y2O3–ZrO2) with particle size of 11–125 μm (Fig. 1-b). In this study, alumina powder with particle size of 40–100 μm (Fig. 1-c) was injected on the coating surface by a powder feeder.

2.2. APS and laser cladding process

Table 1 lists the APS parameters applied in the present study. A powder feed device was used to divide the powder stream...
into four equal streams, which was then driven out by a 4-way coaxial nozzle with four particular powder streams. Argon was utilized as the powder carrier gas. The surface of the coated samples was scanned by a laser beam. The laser was Nd: YAG pulsed laser, model IQL-10 with a mean power of 400 W and standard square shaped pulses. The laser and powder feed parameters used in the present study are listed in Table 2.

2.3. Hot corrosion test

To study the hot corrosion behavior of the applied coatings, a mixture of 55 wt% V$_2$O$_5$ (Merck, Melting Point: 690 °C) and 45 wt% Na$_2$SO$_4$ (Merck, Melting Point: 888 °C) as the corrosive salt was spread over specimens in a concentration of 20 mg/cm$^2$. To avoid the edge effect, the corrosive mixture was kept 5 mm from the edge. The coated samples were then heated in an electric furnace at 1000 °C for of 30 h. Upon heating, the corrosive salt mixture melted on the coating surface. The specimens were then removed from the furnace and cooled naturally in the air.

2.4. Characterization

X-ray diffraction (AW-XDM300, diffractometer with Cu K$_\alpha$ radiation ($\lambda = 1.15406$ nm)) was utilized for phase identification and examination of the corrosion products. The range of 2θ angles was 20–90°, at a scan speed of 0.03°/s. Surface morphology and cross-sectional microstructure were studied to identify the corrosion products and to investigate the corrosion mechanisms. For this purpose, a field emission scanning electron microscope (FESEM; MIRA3-TESCAN, Czech Republic, operated at an accelerating voltage of 15 kV) equipped with an energy dispersive spectroscopy (EDS; SAMX) was used. Image analysis was utilized to study the porosity ratio of the different layers in the TBCs.

The surface roughness (Ra) of the TBC coating was measured by a Mitutoyo Surftest profilometer (Mitutoyo SJ-201P, Japan). The roughness reported is the average of three values scanned from the furnace and cooled naturally in the air.

![Fig. 6. The SEM micrographs of (a) the top surface of the region S and (b) the cross section of the separated layer, (c) the EDS analysis of the region B and (d) the EDS analysis of the region A.](image)
different areas on the coating surface.

To study the mechanical properties (hardness, Young’s modulus, etc.) of the TBCs before and after laser cladding, a nanoindentation Compact Platform with Berkovich indenter was used. The maximum load, the loading and the unloading rates, and the dwell time at the maximum load were 10 mN, 20 mN/min, 20 mN/min and 30 s, respectively.

3. Results and discussion

3.1. Microstructure of the as sprayed and the laser clad coatings

Fig. 2 displays the top surface and cross section of the conventional YSZ applied on the substrate by APS. As obvious in Fig. 2-a, the surface of the APSed coatings has a high roughness ($R_a$) which was measured to be about 9.51 $\mu m$. This high roughness is typical in APSed coating, due to the splats that are deposited on the surface with different flattening parameters [23]. Fig. 2-b shows that the APSed YSZ structure is consisted of columnar grains, formed during directional solidification. The YSZ top coat also contains typical defects such as pores, voids, inter-splat cracks (horizontal cracks between splats) as well as intra-splat cracks (vertical cracks between splats). These defects are considered as penetration paths of the corrosive molten salts which are the main reason for the low hot corrosion resistance of the sprayed TBCs.

Fig. 3 shows the top surface and the cross section of the $Al_2O_3$ laser clad coating. Compared to that of the APSed coating, the surface of the laser clad coating was smooth and denser (Fig. 3-a). The roughness of this surface was measured to be about 7.49 $\mu m$. The typical defects observed in the sprayed coatings are vanished after laser cladding. The porosity ratio of the laser clad coating was measured to be about 4.2%, while this ratio in the YSZ layer was about 11.2%. This is another evidence that the pores can be eliminated by laser cladding treatment. However, still a continuous network of segmented cracks is visible on the surface. These cracks probably were generated because of the small molten pool, fast cooling and localized temperature gradient which generate residual stresses after laser cladding [28,29]. At a higher magnification (Fig. 3-b), it is observed that the cracks are perpendicular to the surface. It has been reported that these cracks increase thermal shocks resistance and are expected to be beneficial for accommodating the oxidation and the mismatch stresses [30].

Fig. 4 shows the XRD patterns of the APSed YSZ and the laser clad layer. Pattern (a) belongs to the YSZ which indicates the presence of $t-ZrO_2$ crystal structure, a common phenomenon after plasma spraying of YSZ. As seen in pattern (b) (The XRD pattern of the $Al_2O_3$ laser clad layer), the dense layer contained $t-ZrO_2$ and the rhombohedral phase of $Al_2O_3$. This pattern confirms the formation of in situ $Al_2O_3$-YSZ composite with the thickness of about 45 $\mu m$ on the top of the sprayed YSZ. This composite probably is formed due to the partial melting of the YSZ layer and mixing with molten alumina during laser cladding. To prove formation of the $Al_2O_3/ZrO_2$ composite layer, Grazing Incidence X-ray Diffraction was utilized (Fig. 4-c).

3.2. Hot corrosion evaluation

The hot corrosion response of the TBCs was studied with SEM, EDS and XRD. Fig. 5, is a macroscopic image of the conventional and the laser clad coating samples after 30 h exposure in the hot corrosion test. As observed, while the conventional YSZ was completely delaminated, no spallation observed in the laser clad coating.

Fig. 6(a and b) demonstrate the TBC failure of the conventional YSZ after the hot corrosion test. It is clear that the spallation occurred in the YSZ/bond coat interface, and the YSZ top layer completely separated from the TBC. Fig. 6-a is a high magnification micrograph of the region S displayed in Fig. 5-a. As observed, the delamination of the YSZ layer has occurred and a wide area of the bond coat has become uncovered. The EDS analyses from regions B and A (Fig. 6C and D), prove that the separated layer and the layer remained on the substrate are YSZ and bond coat, respectively. Fig. 6-b shows the YSZ layer separated from the TBC.

The spallation of TBCs in the YSZ/bond coat interface has been reported by other researchers. Different mechanism are introduced as the TBC failure mechanism, which consists of cracking in the TBC, cracking in the TGO layer near the TBC, or cracking at the TGO-bond coat interface which are caused by the release of the
stored elastic strain energy \[1,31\]. Due to complete spallation in conventional YSZ after 30 h hot corrosion test, the cross sectional observation via SEM was not helpful to see any cracks of TGO. Therefore the authors decided to observe the samples before complete failure to identify if any cracks or TGO have been formed during hot corrosion test. Thus the samples after 18 h hot corrosion test were selected to observe via SEM.

Fig. 7-a shows the high magnification of the TBC in the interface of the bond coat and the YSZ coating after 18 h hot corrosion test. This micrograph clearly shows the delamination mechanism of the YSZ. An interfacial crack has formed in the top coat near the interface of the bond coat and the YSZ, where the EDS result (Fig. 7-b), confirmed the formation of TGO. The effect of the corrosion products and the phase transformation on delamination is discussed at following sections.

Fig. 8(a and b) illustrate the SEM micrographs of the top surface of the conventional YSZ and the laser clad coating, respectively, after the hot corrosion test. As seen, after 30 h of hot corrosion test, rod-type crystals have formed on the conventional YSZ coating. The EDS analysis (Fig. 8-c) proves that this elongated phase is rich in yttrium and therefore is formed as a result of the reaction of yttria with the molten salt at elevated temperature, showing poor resistance of the YSZ coating. In contrast, these elongated features are scarce on the surface of the laser clad coating (Fig. 8-b), proving significant improvement of the hot corrosion resistance of the TBCs after laser cladding of alumina on the surface of YSZ as a result of the formation a dense impermeable layer on the top surface of the YSZ coating. The elimination of the imperfections such as voids and cracks after laser cladding, reduces the penetration paths of molten salts into the YSZ layer. The smooth layer of the TBCs after laser cladding (having lower roughness) also decreases the effective contact surface between the YSZ and the molten corrosive salts. The fact that no
Delamination and spallation occurred in the laser clad coating due to the dense composite layer on the top surface of TBC, which not only sealed the penetration paths of the molten salts, but also decreased the oxygen diffusion and formation of a TGO layer. The results of EDS analysis of A and B areas in Fig. 8-a show that the rod shaped crystals (the region A) contain O, V and Y and the region B contains O, Y, Zr.

XRD patterns support the EDS analysis and SEM micrographs. Fig. 9 shows the XRD results of the conventional YSZ and the laser clad coating after hot corrosion test. Pattern (a) belongs to the conventional YSZ. It is obvious from this pattern that after hot corrosion test, the conventional YSZ contains phases such as t-ZrO$_2$ and YVO$_4$ (rod shaped crystals in Fig. 8). Peaks of m-ZrO$_2$ and YVO$_4$ (as corrosion products) are so sharp in this pattern which is indicative of the low hot corrosion resistance of the coating. Pattern (b) is the XRD analysis of the laser clad coating after the hot corrosion test. The corrosion products are also present in this pattern, however, the peaks in the pattern of laser clad coating are shortened which indicates the improved hot corrosion resistance of the TBC after laser cladding. The peak intensity of YVO$_4$ before laser cladding is almost 2 times of peak intensity after laser cladding. It was mentioned earlier that during reactions between yttria and the molten salts, yttria will be leached out from the YSZ, resulting in destabilization of the t-ZrO$_2$ and formation of the m-ZrO$_2$. This transformation is accompanied by a large destructive volume change [5]. The stresses resulting from the volume change cause the delamination and spalling of the coating.

In order to quantitatively compare the hot corrosion resistance of the conventional YSZ and the laser clad coating, the amount of m-ZrO$_2$ (known as a very important criterion for TBCs destabilization) was measured in both coatings using the XRD patterns. Following equation was utilized to calculate the percentage of the undesirable m-ZrO$_2$ phase volume fraction [32]:

$$m_{\text{ZrO}_2} = \frac{I_m(111) + I_m(111)}{I_m(111) + I_m(111) + I_t(111)} \times 100$$

where, $I_m$ represents the diffraction intensity of the respective
lattice planes and \( \theta \) is the peak intensity of \( \gamma'\)-ZrO\(_2\) from (111) plane. Fig. 10 demonstrates the \( \gamma'\)-ZrO\(_2\) and m-ZrO\(_2\) peaks more specifically in the conventional YSZ and the laser clad coatings. In this way the volume percent of the m-ZrO\(_2\) formed in the coatings after hot corrosion test was calculated to be about 70% for the conventional YSZ and about 13% for the laser clad coatings, which proves the significant improvement of the hot corrosion resistance of the TBCs after alumina laser cladding.

3.3. Mechanical properties of THE TBCs before and after laser cladding

Fig. 11 illustrates the load-displacement curves of TBC before and after laser cladding. The average value of different parameters obtained from Fig. 11, are given in Table 3. The \( S \) parameter is the slope of curves \( (dp/dh) \) upon unloading. E and H are Young’s modulus and hardness, respectively. As obvious from Table 3, the \( E/H \) values for TBC after laser cladding increased compared to that of the conventional YSZ due to the existence of alumina in the laser clad layer.

4. Conclusions

Alumina laser cladding of air plasma sprayed YSZ on the in738LC was successfully performed in the current investigation. Hot corrosion behavior of both coatings was evaluated at 1000 °C for 30 h in the presence of a mixture of 55 wt% V\(_2\)O\(_5\) +45 wt% Na\(_2\)SO\(_4\) molten salts. The following conclusions may be drawn from the investigation:

1. An Al\(_2\)O\(_3\)/ZrO\(_2\) rigid composite layer with the thickness of about 45 \( \mu \)m was formed on the surface of the YSZ top coat.
2. APSed typical defects such as pores, voids, inter- and intra- splat cracks were eliminated after laser cladding and a dense, smooth and impermeable layer was formed on the surface.
3. Due to the reaction of the molten salts with yttria, the stabilizer was leached out of the zirconia solid solution, resulting in destabilization of the zirconia from the tetragonal to the monoclinic phase and therefore the destruction of the coating.
4. VVO\(_4\) rod shaped crystals were formed on the surface of the coatings as the corrosion products.
5. After the hot corrosion test of the conventional YSZ, a TGO layer was formed in the bond coat/top coat interface and cracks were observed on the YSZ top coat near the TGO layer.
6. The structural transformation of zirconia, formation of VVO\(_4\) and cracks led to the complete delamination of the conventional YSZ and failure of TBC.
7. The amount of the undesirable monoclinic zirconia in the conventional YSZ was about 70%, while that of the laser clad coating was about 13%, which is indicative of a considerable improvement in hot corrosion resistance of the TBCs after laser cladding.

References