Research Article
The Role of Nanostructured Al$_2$O$_3$ Layer in Reduction of Hot Corrosion Products in Normal YSZ Layer

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YVO$_4$ crystals and monoclinic ZrO$_2$ are known as hot corrosion products that can considerably reduce the lifetime of thermal barrier coatings during service. The hot corrosion resistance of two types of air plasma sprayed thermal barrier coating systems was investigated: an Inconel 738/NiCrAlY/YSZ (yttria-stabilized zirconia) and an Inconel 738/NiCrAlY/YSZ/nano-Al$_2$O$_3$ as an outer layer. Hot corrosion test was accomplished on the outer surface of coatings in molten salts (45% Na$_2$SO$_4$ + 55% V$_2$O$_5$) at 1000°C for 52 hour. It was found that nanostructured alumina as outer layer of YSZ/nano-Al$_2$O$_3$ coating had significantly reduced the infiltration of molten salts into the YSZ layer and resulted in lower reaction of fused corrosive salts with YSZ, as the hot corrosion products had been substantially decreased in YSZ/nano-Al$_2$O$_3$ coating in comparison with normal YSZ coating after hot corrosion process.

1. Introduction

Thermal barrier coatings (TBCs) are extensively used to protect turbine blades against high temperature oxidation and corrosion. The TBC systems usually consist of an MCrAlY bond coat (M = Ni and/or Co) as an oxidation-resistant layer, yttria-stabilized zirconia (YSZ) as a thermally insulating ceramic top coat, and a substrate (Ni-based superalloy) [1–5]. Unfortunately, TBCs fail during service due to oxidation, hot corrosion, and phase transformation which considerably decrease the durability of the coating [4, 6]. Low-quality fuels usually contain impurities such as Na and V which can form Na$_2$SO$_4$ and V$_2$O$_5$ corrosive salts on the coating of turbine blades [7, 8]. These fused corrosive salts can penetrate into the entire thickness of the YSZ through splat boundaries and other YSZ coating defects such as microcracks and open pores [8]. The penetrated salts can then react with yttria (the stabilizer component of YSZ) and depletion of the stabilizer and phase transformation of tetragonal zirconia to monoclinic zirconia can occur in a very rapid and effective manner during cooling [7, 8]. This phase transformation is also accompanied by 3–5% rapid volume expansion, leading to cracking and spallation of TBCs [9].

It was found that the presence of a dense Al$_2$O$_3$ layer over the YSZ coating in atmospheric plasma sprayed TBCs can considerably reduce the molten salts diffusion into the YSZ layer and results in higher TBC resistivity against hot corrosion [7, 8]. It can be said that a layered composite TBC containing alumina component can considerably prevent hot corrosion [7]. It is interesting to note that Al$_2$O$_3$ cannot be dissolved within the ZrO$_2$. The alumina (as a rigid matrix) can only surround the ZrO$_2$ particles in TBC system. This phenomenon could create local compressive stresses which could prevent the phase transformation of tetragonal zirconia to monoclinic phase [8, 10, 11]. Hence, the main purpose of this research is to improve the hot corrosion resistance of normal TBCs using nanoalumina as a third layer in TBC system. Two types of air plasma sprayed TBC systems were investigated: an Inconel 738/NiCrAlY/normal YSZ, and an Inconel 738/NiCrAlY/normal YSZ/nano-Al$_2$O$_3$ systems. Investigation also includes microstructural characterization of TBCs before and after hot corrosion test.
2. Experimental Procedures

2.1. As-Received Materials. Nickel-based superalloy (Inconel 738) squares of $25 \times 25 \times 6$ mm were grit blasted with alumina particles and were then used as substrate. Three types of commercial powders were selected: Amdry 962 (Ni-22Cr-10Al-1Y, $-106 + 52 \mu m$) as bond coat, Metco 204 NS-G ($ZrO_2 - 8\% Y_2O_3$, $-106 + 11 \mu m$), and Inframat LLC 0802 (nano-$\alpha$-$Al_2O_3$ with high purity, 80 nm) as TBC or ceramic layer.

2.2. Granulation of Nano-$Al_2O_3$ Powders. It is worth mentioning that, during air plasma spraying, nanopowders (particularly nano ceramic powders) could adhere to the walls of the feeding system making it extremely difficult to move them towards the plasma torch due to their high specific area and low mass. In order to overcome this problem, reconstitution of the nanoparticles into micrometer-sized granules, a process known as granulation treatment, is essential. In this regard, researchers found that the most favorable granule size...
is in the range of 10 μm–110 μm [12–15]. A dense nanoceramic coating can be produced by using granulated nanopowders which have excellent flow ability and high apparent density [15]. Hence, nano-Al₂O₃ powders with an average particle size nominally less than 80 nm and PVA (poly-vinyl alcohol as a binder) were used as starting materials. In this method, 50 g of PVA was dissolved in 80 mL of distilled water at 200°C using a magnetic stirrer. At the same time, the nano-Al₂O₃ particles were dispersed in distilled water by using an ultrasonic machine for 30 min at 60°C. The dispersed nano-Al₂O₃ solution was then added to the PVA solution with the aid of a magnetic stirrer at 250°C for 45 min. The water from the solution was removed using a rotary-evaporator device, in order to prevent phase segregation [13]. These granulated powders were dried using a normal electric furnace at 200°C for 145 min.

Agglomerated powders were then sieved through 150 μm, 100 μm, and 50 μm meshes, in order to obtain an adequate shape and suitable size for plasma spraying. The final particle size of the granulated nano-Al₂O₃ powders used for air plasma spraying was estimated to be 80–100 μm [16].

2.3. Air Plasma Sprayed Coatings for Hot Corrosion Test. Two types of coatings were produced by air plasma spray (APS) method: the normal YSZ and the layer composite of YSZ/nano-Al₂O₃ as outer layer coatings. Table 1 lists the thickness of coatings, while Table 2 shows the parameters of air plasma spraying method.

2.4. Hot Corrosion Test. A mixture of 55 wt% V₂O₅ and 45 wt% Na₂SO₄ powders (see Figure 1) was spread on the outer surface of the coatings with 30 mg/cm² concentration. To prevent edge corrosion effect, a 4 mm gap from the uncoated edge was spared for all the coatings. The samples were then put in a normal electric furnace with air atmosphere at 1000°C for 52 hr and then cooled down until ambient temperature was reached inside the furnace. These samples were also intermittently checked every 4 hr cycle during the hot corrosion exposure.

2.5. Microstructural Characterization of Coatings. The microstructural characterization of the surface and the
cross-section of the coatings before and after hot corrosion test were carried out using field emission scanning electron microscopy (FESEM) and scanning electron microscopy (SEM) equipped with energy dispersive spectrometer (EDS). An X-ray diffraction (XRD) device was used to determine the type of corrosive phases formed on the YSZ layer of TBCs after hot corrosion test at 1000°C.

3. Results and Discussion

3.1. Morphology Investigation of the Granulated Nano-Al₂O₃ Powders. Figure 2(a) exhibits the morphology of nano-Al₂O₃ powders after granulation treatment. It can be observed that (see Figures 2(b) and 2(c)) there are a high number of nano-Al₂O₃ grains in a granulated particle which can be considered as a plasma sprayable powder in APS method.

### Table 2: Parameters of air plasma spraying (APS) method.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NiCrAlY</th>
<th>YSZ</th>
<th>Granulated nano-Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (A)</td>
<td>450</td>
<td>550</td>
<td>500</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>50</td>
<td>70</td>
<td>50</td>
</tr>
<tr>
<td>Primary gas, Ar (L/min)</td>
<td>85</td>
<td>38</td>
<td>85</td>
</tr>
<tr>
<td>Secondary gas, H₂ (L/min)</td>
<td>15</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>Powder feed rate (g/min)</td>
<td>15</td>
<td>35</td>
<td>25</td>
</tr>
<tr>
<td>Spray distance (cm)</td>
<td>15</td>
<td>7.5</td>
<td>10</td>
</tr>
</tbody>
</table>

3.2. Microstructural Characterization of Air Plasma Sprayed Coatings. Figure 3 demonstrates the cross-sections of two types of as-sprayed TBCs. All the coatings display a lamellar structure which is a characteristic of plasma sprayed coatings [1–5]. Figure 3(a) shows composite of YSZ/nano-Al₂O₃ as an outer layer on the bond coat after air plasma spraying. On the other hand, Figure 3(b) indicates normal YSZ layer on the NiCrAlY layer indicating that is the normal TBC system.

The morphology of as-sprayed nano-Al₂O₃ layer was characterized using FESEM equipped with EDS as shown in Figure 4. It shows that dense nanostructured Al₂O₃ coating has lower pinholes, voids and microcracks compared to those of normal YSZ coating, as shown in Figure 5.

It can be predicted that nano-Al₂O₃ layer over YSZ coating will considerably prevent the infiltration of molten salts into the YSZ layer during hot corrosion test at elevated temperatures (see Figure 4).

### Table 1: Thickness of layers (µm) in two types of thermal barrier coating systems.

<table>
<thead>
<tr>
<th>Type of TBC</th>
<th>NiCrAlY</th>
<th>YSZ</th>
<th>Granulated nano-Al₂O₃</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>207.3 ± 3.2</td>
<td>392.9 ± 11.8</td>
<td>—</td>
<td>YSZ coating</td>
</tr>
<tr>
<td>Nanolayer composite</td>
<td>216.5 ± 6.3</td>
<td>215.4 ± 5.1</td>
<td>102.8 ± 4.5</td>
<td>YSZ/nano-Al₂O₃ coating</td>
</tr>
</tbody>
</table>

*YSZ: yttria stabilized zirconia.
coating surface appears porous and destroyed with many cracks and crystals deposited (as one of the hot corrosion products) on the surface (Figures 6(a), 6(b), and 6(c)). Figure 7 also shows the surface of YSZ as inner layer of YSZ/nano-Al$_2$O$_3$ coating after hot corrosion test at 1000°C.

The detrimental crystals are rod shaped. In the normal YSZ their sizes are larger (80–85 µm) and thicker (2.5–3 µm) (Figure 6(c)) compared to thinner rod crystals (0.5–1.5 µm) with low number and small size (15–20 µm) in YSZ/nano-Al$_2$O$_3$ coating (Figure 7(c)). The EDS analysis (see Figure 8) indicated that the rod crystals are mainly composed of yttrium, vanadium, and oxygen. X-ray diffraction analysis identified these crystals as YVO$_4$.

The XRD analysis performed on the YSZ layer of the coatings after hot corrosion test produced results of XRD patterns as shown in Figure 9. Formation of monoclinic ZrO$_2$ and YVO$_4$ crystals was detected on the surface of all the coatings after exposure to molten salts at 1000°C, but the intensity of their peaks was totally different. Monoclinic zirconia is an unstable phase. This phase will be transformed to tetragonal zirconia phase at approximately 1000°C. This tetragonal phase will transform back to monoclinic zirconia phase during cooling which is accompanied by 3–5% volume expansion and finally leads to the spallation of TBC during subsequent thermal cycles of hot corrosion test [10, 17, 18].
Using (1) \[8, 19, 20\], the monoclinic zirconia volume fractions \(V_m\) % in the two types of TBCs after hot corrosion test were calculated:

\[
V_m\% = \frac{M_1 + M_2}{M_1 + M_2 + T} \times 100. \tag{1}
\]

\(M_1\) and \(M_2\) are the intensity of monoclinic \(\text{ZrO}_2\) (1 1 1) and (1 1 1) peaks, respectively, and \(T\) is the intensity of tetragonal \(\text{ZrO}_2\) (1 0 1) peak in XRD patterns after hot corrosion test. The volume fractions of monoclinic zirconia phase \(V_m\) % in the two types of TBCs are compared as shown in Figure 10. This figure demonstrates that the volume fraction of monoclinic \(\text{ZrO}_2\) has been reduced from 66% in normal YSZ to 15% in YSZ as inner layer of YSZ/nano-\(\text{Al}_2\text{O}_3\) coating. This result indicates that phase transformation of tetragonal zirconia to monoclinic zirconia in YSZ/nano-\(\text{Al}_2\text{O}_3\) coating during cooling is lower compared to normal YSZ coating.

The comparison of XRD results (see Figure 9) indicates that the intensity of principal peak of \(\text{YVO}_4\) in normal YSZ is considerably higher compared to \(\text{YSZ}\) as inner layer of YSZ/nano-\(\text{Al}_2\text{O}_3\) coating. This phenomenon can also be confirmed by measuring the length of the \(\text{YVO}_4\) rod-shaped crystals. Figure 11 shows that the average length of rod crystals of \(\text{YVO}_4\) in YSZ as inner layer of YSZ/nano-\(\text{Al}_2\text{O}_3\) coating has been substantially reduced compared to normal YSZ coating after hot corrosion test at 1000°C.

3.4. The Mechanism of Monoclinic Zirconia and \(\text{YVO}_4\) Crystals Formation as Hot Corrosion Products in the YSZ Layer. The mechanism of monoclinic zirconia and \(\text{YVO}_4\) crystals formation as hot corrosion products during corrosion process can be explained by the following reactions:

\[
\text{Na}_2\text{SO}_4 (l) \rightarrow \text{Na}_2\text{O} (l) + \text{SO}_3 (g) \tag{2}
\]

\[
\text{Na}_2\text{O} (l) + \text{V}_2\text{O}_5 (l) \rightarrow 2\text{NaVO}_3 (l) \tag{3}
\]

\[
\text{V}_2\text{O}_5 (l) + \text{Na}_2\text{SO}_4 (l) \rightarrow 2\text{NaVO}_3 (l) + \text{SO}_3 (g) \uparrow \tag{4}
\]

\[
\text{ZrO}_2 \left( \text{Y}_2\text{O}_3 \right) (s) + 2\text{NaVO}_3 (l) \rightarrow \text{ZrO}_2 \text{ (monoclinic)} (s) + 2\text{YVO}_4 (s) + \text{Na}_2\text{O} (l) \tag{5}
\]

\[
\text{ZrO}_2 \left( \text{Y}_2\text{O}_3 \right) (s) + \text{V}_2\text{O}_5 (l) \rightarrow \text{ZrO}_2 \text{ (monoclinic)} (s) + 2\text{YVO}_4 (s) \tag{6}
\]

According to reactions (2)–(4), \(\text{NaVO}_3\) was formed at elevated temperatures (see Figure 12). \(\text{NaVO}_3\) then reacted with \(\text{Y}_2\text{O}_3\) to generate monoclinic \(\text{ZrO}_2\), \(\text{YVO}_4\), and \(\text{Na}_2\text{O}\) (reaction (5)) \[21–24\]. On the other hand, it has been reported that \[21, 22\] \(\text{V}_2\text{O}_5\) can react directly with \(\text{Y}_2\text{O}_3\) (stabilizer component of zirconia) to produce monoclinic \(\text{ZrO}_2\) and \(\text{YVO}_4\) crystals as hot corrosion products (reaction (6)).

Chen et al.’s investigation \[11\] on hot corrosion of plasma sprayed \(\text{Al}_2\text{O}_3\) and \(\text{ZrO}_2\) coatings in molten \(\text{Na}_2\text{SO}_4\) showed that \(\text{NaAlO}_2\) can be formed on the surface of \(\text{Al}_2\text{O}_3\) particles (reactions (2), (7)). Hot corrosion rate of \(\text{Al}_2\text{O}_3\) coating in molten \(\text{Na}_2\text{SO}_4\) was much lower compared to normal \(\text{ZrO}_2\) coating. In this research \(\text{NaAlO}_2\) was detected by XRD analysis (see Figure 9(b)) and, as such, it can be said that,
the $\text{Al}_2\text{O}_3$ layer is generally protected by $\text{NaAlO}_2$ compound during hot corrosion process:

$$\text{Al}_2\text{O}_3 (s) + \text{Na}_2\text{O} (l) \rightarrow 2\text{NaAlO}_2 (s)$$  \hspace{1cm} (7)

$\text{Na}_2\text{SO}_4$ is known as an accelerator factor of chemical reactions during hot corrosion [25, 26]. It was found that $\text{NaVO}_3$ with relatively low melting point (630°C) [27] will be able to increase the phase transformation of tetragonal $\text{ZrO}_2$ to monoclinic $\text{ZrO}_2$ during hot corrosion test (reaction (5)) due to the depletion of stabilizer ($\text{Y}_2\text{O}_3$) component of the YSZ coating.

### 3.5. Hot Corrosion Behavior of Two Types of Thermal Barrier Coatings

The hot corrosion behavior of thermal barrier coatings in this research can be explained by the following steps: (a) molten salts penetrate into the YSZ layer; (b) molten salts react with $\text{Y}_2\text{O}_3$ (stabilizer component of zirconia); (c) tetragonal zirconia will be transformed to monoclinic zirconia phase; and (d) formation of large rod-shaped $\text{YVO}_4$ crystals with an average length of 85 $\mu$m and outward growth (see Figure 13) in normal YSZ coating which can impose additional stresses to the system. The spallation of normal YSZ coating will occur at the NiCrAlY/YSZ interface due to those supplementary stresses in the coating.

In the meantime, premature YSZ spallation is a result of the formation of large monoclinic $\text{ZrO}_2$ and $\text{YVO}_4$ crystals (see Figure 13) at the bond coat/normal YSZ interface, while, in YSZ/nano-$\text{Al}_2\text{O}_3$ coating, the least amount of molten salts infiltrated through nanoalumina layer towards the YSZ coating and reacted with YSZ at the interface of YSZ/nano-$\text{Al}_2\text{O}_3$. It can be said that due to its short length of about 15–20 $\mu$m the $\text{YVO}_4$ small crystals did not play a substantial role in the spallation of YSZ coating. However, the spallation of nano-$\text{Al}_2\text{O}_3$ layer is mainly related to the formation of monoclinic $\text{ZrO}_2$ (15%) at the interface of YSZ/nano-$\text{Al}_2\text{O}_3$ during hot corrosion test at 1000°C. It can be concluded that the linked pinholes and microcracks can provide the pathways for molten salts infiltration into the coating during hot corrosion process. However, in this research, the dense nanostructured $\text{Al}_2\text{O}_3$ layer could significantly prevent the diffusion of molten salts in YSZ layer due to the compactness of the nanostructure. Therefore the amount of monoclinic $\text{ZrO}_2$ and $\text{YVO}_4$ crystals was substantially lessened in YSZ/nano-$\text{Al}_2\text{O}_3$ coating in comparison with normal YSZ coating after hot corrosion test.

### 4. Conclusions

Reaction of molten salts containing $\text{NaVO}_3$ with $\text{Y}_2\text{O}_3$ (as stabilizer component of $\text{ZrO}_2$) led to the formation...
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YSZ as inner layer of YSZ/nano-Al₂O₃ coating

ZrO₂
200 𝜇m (a)

YVO₄ small crystals

ZrO₂
20 𝜇m (b)

YVO₄ small crystals

50 𝜇m (c)

Figure 7: Surface morphology of YSZ layer of nano-TBC system after hot corrosion test at different magnifications: (a) 100x, (b) 200x, and (c) 400x.

Figure 8: EDS analysis from rod crystals of YVO₄ on the YSZ layer of TBC systems: (a) large rod crystals of YVO₄ on the YSZ layer of normal TBC system and (b) small rod crystals of YVO₄ on the YSZ layer of nano-TBC system.

of monoclinic ZrO₂ and YVO₄ crystals (as hot corrosion products) on the YSZ layer during hot corrosion test. This phenomenon finally led to the separation of YSZ layer from the bond coat after 12 hr. It was found that a dense nano-Al₂O₃ layer with lower pinholes can significantly prevent the infiltration of molten salts into YSZ layer and therefore the amount of monoclinic ZrO₂ and YVO₄ crystals was considerably reduced in YSZ/nano-Al₂O₃ coating in comparison with normal YSZ coating. This phenomenon had caused the separation of nano-Al₂O₃ layer from the YSZ coating after 52 hr. In other words, the nanostructured Al₂O₃ layer could maintain YSZ coating as main component of TBC systems during hot corrosion test due to lower formation of monoclinic ZrO₂ (15%) at the interface of YSZ/nano-Al₂O₃ coating. Meanwhile, the average length of YVO₄ rod crystals in YSZ as inner layer of YSZ/nano-Al₂O₃ coating was lower compared to that of normal YSZ coating after hot corrosion test.
Figure 9: XRD patterns of (a) normal YSZ layer of normal TBC system and (b) YSZ as inner layer of YSZ/nano-Al$_2$O$_3$ coating after hot corrosion test at 1000°C.

Figure 10: Volume fraction of monoclinic zirconia in the coatings after hot corrosion test.

Figure 11: Length average of rod crystals of YVO$_4$ in two types of TBCs after hot corrosion test at 1000°C.
Figure 12: EDS analysis of NaVO₃ compound on the YSZ layer after hot corrosion test at 1000°C.

Figure 13: Formation of monoclinic ZrO₂ and YVO₄ large crystals which have outward growth in the normal YSZ layer.

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References


