A preliminary study of the oxidation behavior of TBC with cold spray CoNiCrAlY bond coat
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Cold gas dynamic spray (CGDS) utilizes a supersonic gas jet to accelerate fine solid powders above a critical velocity at which particles impact, deform plastically, and bond to the substrate material in the ambient environment. This process is potentially beneficial for thermal barrier coating (TBC) bond coat deposition because it would avoid oxidation of the feedstock powder that normally occurs when higher temperature thermal spray processes are employed. Therefore, there would be no prior aluminum depletion in as-deposited bond coats produced by the CGDS technique. This paper presents the oxidation behaviour of a TBC with CGDS-produced CoNiCrAlY bond coat, in comparison with TBCs with APS- and HVOF-CoNiCrAlY bond coats. Oxidation behaviors of these TBCs were evaluated in terms of microstructural evolution, kinetics of thermally-grown-oxides (TGO), as well as cracking behaviour during thermal exposure at 1050 °C.

1 Introduction

In a thermal barrier coating (TBC) system, the metallic bond coat (BC) plays the role of enhancing the adhesion of the ceramic topcoat (TC) to the substrate and protecting the substrate metal from oxidation and corrosion. When exposed at high temperatures, oxidation of the bond coat results in the formation of a thermally grown oxide (TGO) layer at the ceramic/bond coat interface. This layer acts as a diffusion barrier during the extended thermal exposure in service, thus protecting the substrate from further oxidation. However, growth of the TGO tends to increase the internal stress within the TBC system and causes cracking in the TC/BC interfacial region, which eventually leads to spallation of the topcoat [1-5].

In previous studies on TBCs with thermal spray bond coats, it was found that the growth of the TGO layer first proceeded in a parabolic manner, which was then followed by an accelerated growth stage [6-9]. It was shown that TGO growth was dependent on the thermal spray processes [8]. A power-law relationship between the maximum crack length and TGO thickness was observed in recent studies [9-11].

In recent years, cold gas dynamic spray (CGDS) deposition of metallic bond coats has been studied [12-18], because of its faster deposition rate and lower deposition temperature as compared to the traditional thermal spray techniques. This work investigates the influence of various bond coat deposition processes, including air plasma spray (APS), high velocity oxygen fuel (HVOF), and, in particular, CGDS, on the oxidation performance of TBCs with a Co-32Ni-21Cr-8Al-0.5Y (wt.%) bond coat.

2 Experimental

The TBCs consisted of a CoNiCrAlY bond coat and a ZrO$_2$-8wt.%Y$_2$O$_3$ topcoat. The bond coat was deposited to a thickness of 140-180 µm by either the APS, HVOF or CGDS technique with powders of Co-32Ni-21Cr-8Al-0.5Y (wt.%), onto φ16 mm × 10 mm Inconel 625 disks. On top of the CoNiCrAlY, the topcoat was deposited to a thickness of 250-280 µm by the APS technique, with powders of ZrO$_2$-8wt.%Y$_2$O$_3$. The spray techniques and feedstock are described in Table 1. Both BC and TC were produced based on the spray parameters recommended by the manufacturers of the torch and feedstock except for the CGDS BC for which the spray parameters where adjusted to attain a compromise between the faster particle velocity using nitrogen as propelling gas and preventing clogging of the MOC24 nozzle because of a too high gas temperature. The inlet gas pressure and temperature were thus 40 bar and 700°C respectively. No heat treatment was applied to the TBCs prior to thermal exposure.

<table>
<thead>
<tr>
<th>Table 1. Spraying techniques and feedstock</th>
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<tr>
<td>Bond coat</td>
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<td>APS</td>
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<tr>
<td>HVOF</td>
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<tr>
<td>CGDS</td>
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<tr>
<td>Topcoat</td>
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</table>

All TBC specimens were subjected to thermal cycling in air, which consisted of 10-15-minute ramping, 100-hour holding at 1050°C, and >40-minute cooling to the ambient temperature (25°C). The oxidized samples were sectioned after completion of a predetermined number of thermal cycles that resulted in thermal exposure times between 100 and 1000 hours. The sections were mounted using epoxy, and mechanically polished. The specimens were then examined using a Philips XL30S FEG scanning electron microscope (SEM) with an energy-dispersive spectrometer (EDS). The area and length of TGO, as well as the crack length in the TBC, were measured using ImageTool software, based on the micrographs taken from the cross sections of the tested samples. The TGO area was measured by drawing a polygon along the ceramic/TGO and TGO/bond coat interfaces, while the TGO length was determined by drawing a line as short as possible along the TGO. From each specimen, 20-70 micrographs were taken.
for the TGO measurement. The various oxides were identified by SEM-EDS.

3 Results and discussion

3.1 Coating microstructures

The ceramic topcoats on all the TBC specimens were uniformly deposited using the APS technique. The typical topcoat microstructure contained porosity and splat boundaries, which present as crack-like discontinuities (Fig. 1). The maximum dimension of the crack-like discontinuities in the ceramic topcoat was in the range of 70-100 µm. The as-sprayed APS-CoNiCrAlY contained segmented Al₂O₃ veins (Fig. 1a) within the bond coat as well as at the TC/BC interface. A semi-quantitative SEM/EDS analysis showed that the aluminum concentration was highly non-uniform in the as-sprayed APS bond coat, with some regions having very low Al content (Table 2), compared to that in the CoNiCrAlY powder (≈16 at.%). This non-uniformity of Al distribution in the bond coat can probably be attributed to the preferential oxidation and/or vaporization in the plasma, because the particle surface temperature was much higher than the melting point of the CoNiCrAlY.

The as-sprayed HVOF-CoNiCrAlY (Fig. 1b) was rather uniform and contained much less oxide as compared to the APS-CoNiCrAlY (Fig. 1a). A semi-quantitative SEM/EDS analysis showed that the aluminum concentration in HVOF-CoNiCrAlY at the TC/BC interface was much higher than that in APS-CoNiCrAlY.

The as-sprayed CGDS-CoNiCrAlY (Fig. 1c), on the other hand, contained some discontinuities such as splat boundaries, but no oxide could be observed within the bond coat or at the TC/BC interface.

Table 2. Aluminum concentrations in the bond coats

<table>
<thead>
<tr>
<th>Bond Coat</th>
<th>at.% Al</th>
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<tr>
<td>APS-CoNiCrAlY</td>
<td>9.6-17.9</td>
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<tr>
<td>HVOF-CoNiCrAlY</td>
<td>14.7-23.2</td>
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<tr>
<td>CGDS-CoNiCrAlY</td>
<td>15.4-20.8</td>
</tr>
</tbody>
</table>

3.2 Oxidation of TBC with CoNiCrAlYs

Upon thermal exposure in air, a layer of mixed oxides, predominantly (Cr,Al)_2O₃+(Co,Ni)(Cr,Al)_2O₄ (CS), formed along the interface between the ceramic topcoat and the bond coat (Fig. 2a) in the APS-CoNiCrAlY. The Al₂O₃ portion in this oxide layer was apparently less than 20%. At the same time, clusters of chromia, spinel and nickel oxide, abbreviated as CSN, also formed at the ceramic/bond coat interface. As such, the TGO formed in the APS-CoNiCrAlY consisted of a CS layer and CSN clusters.

As thermal exposure continued, the TGO layer grew thicker (Fig. 2b), and in the meantime, pre-existing crack-like discontinuities in the ceramic developed into fully open cracks. Extensive crack propagation in the ceramic topcoat and associated with the CSNs was also observed after 600 hours (Fig. 2c). The APS-CoNiCrAlY-TBC failed after 700 hours.

Fig. 1. Microstructures of as-sprayed (i.e., no vacuum heat treatment applied) TBCs with (a) APS- (b) HVOF- and (c) CGDS-CoNiCrAlY bond coat.

The TGO formed in the HVOF-CoNiCrAlY was composed of a layer of predominantly Al₂O₃ and some scattered clusters of alumina, spinel and nickel oxide (ASN) and CSNs (Fig. 3a). Opening of pre-existing discontinuities also occurred in the HVOF-CoNiCrAlY-TBC after extended thermal exposure, which led to formation of long cracks via crack propagation and
coalescence in the ceramic topcoat, (Fig. 3b). The HVOF-CoNiCrAlY failed after 5000 hours.

Fig. 2. As-sprayed APS-CoNiCrAlY shows (a) a TGO layer of chromia+spinel with CSNs after 100 hours, (b) discontinuity opening after 300 hours, and (c) crack propagation and coalescence associated with the TGO after 600 hours.

Similar to the HVOF-CoNiCrAlY, CGDS-CoNiCrAlY developed a TGO that was composed of a layer of predominantly $\text{Al}_2\text{O}_3$, as well as some ASNs and CSNs (Fig. 4a); however, the CSNs in the CGDS-CoNiCrAlY were apparently much less than in the HVOF-CoNiCrAlY. After extended thermal exposure, opening of pre-existing discontinuities also occurred in the CGDS-CoNiCrAlY-TBC, which led to crack propagation and coalescence, forming longer cracks in the ceramic (Fig. 4b). Failure of the CGDS-CoNiCrAlY was not observed after 1800 hours, and thermal exposure is still in progress.

Fig. 3. As-sprayed HVOF-CoNiCrAlY shows (a) a TGO layer of predominantly alumina with ASN and CSN clusters after 100 hours, (b) a discontinuity in the ceramic/bond coat interface region developed into a crack after 1000 hours.

3.3 TGO growth and crack propagation in the TBCs

To take into account the entire TGO, an equivalent TGO thickness, $\delta_{eq}$, is defined as [19]:

$$\delta_{eq} = \frac{\Sigma (\text{cross sectional TGO area})}{\Sigma (\text{cross sectional length of TC/BC interface})}$$  \hspace{1cm} (1)

Use of this approach was due to the rough TC/BC interface, as well as heterogeneous TGO growth especially when ASN and CSN clusters were formed between the ceramic topcoat and the bond coat (Figs. 2-4). The relationship between $\delta_{eq}$ and exposure time (Fig. 5) shows a parabolic TGO growth with HVOF- and CGDS-CoNiCrAlYs, which is consistent with some previous observations [20-23], and a three-
stage TGO growth with APS-CoNiCrAlY which is quite similar to that observed in a thermal cyclic test [9].

Fig. 4. As-sprayed CGDS-CoNiCrAlY shows (a) a TGO layer of predominantly alumina with ASN and CSN clusters between the ceramic topcoat and alumina layer after 100 hours, (b) the increased thickness of the TGO and a discontinuity in the ceramic/bond coat interface region developed into a crack after 1000 hours.

It can also be seen that both HVOF- and CGDS-CoNiCrAlYs had higher TGO growth rates than the APS-CoNiCrAlY at the very beginning of the thermal exposure; however, the latter exhibited an accelerated TGO growth after 400 hours (Fig. 5), leading to TBC failure. At this point, aluminum deletion would reach a critical point such that heterogeneous oxidation would occur underneath the TGO, leading to the onset of accelerated TGO growth [9].

The maximum crack size (found in all viewing sections of the coating) was chosen as the parameter to evaluate the cracking behaviour in the TBCs examined. In general, the maximum crack length in a TBC increased as the exposure time increased (Fig. 6). It may be noticed that cracks propagated faster in the APS-CoNiCrAlY-TBC specimens than in the HVOF-, and CGDS-CoNiCrAlY-TBCs. Plotting the maximum crack length as a function of TGO thickness (Fig. 7) reveals that log(\(a_{\text{max}}\)) versus log(\(\delta_{\text{eq}}\)) has a nearly linear relationship, suggesting that the relationship between the maximum crack length in the TBC and TGO thickness can be expressed by a power law. However, the \(a_{\text{max}}\)-\(\delta_{\text{eq}}\) relationship for APS-, HVOF- and CGDS-CoNiCrAlY are quite different. This can be attributed to the different aluminum concentrations, which would affect the type and quantity of TGO, as well as the interface structure and residual stress state as produced by the different deposition techniques.

By comparison, the CGDS-CoNiCrAlY appeared to have the lowest TGO growth up to 1000 hours of thermal exposure at 1050°C (Fig. 5), and the crack propagation behavior was comparable with HVOF-CoNiCrAlY (Fig. 6). Both are much lower than APS-CoNiCrAlY.

It has been shown that the critical crack size for initiating TBC spallation is somehow related to the topcoat thickness [24]. It is possible that TBCs with different topcoat thickness values would fail at different TGO thickness levels. As such, understanding of the relationship between crack...
length and TGO thickness, as well as the influence of spraying process on such a relationship, may be valuable for TBC life prediction. The nature of such a relationship merits further investigation via both numerical and experimental studies.

Fig. 7. The maximum crack length as a function of TGO thickness in TBCs with CoNiCrAlY bond coats.

4 Conclusions

In the present work, TGO growth behaviour and cracking behaviour were studied in TBC systems with APS-, HVOF- and CGDS-CoNiCrAlY bond coats during thermal exposure.

It was observed that in APS-CoNiCrAlY the TGO exhibited a three-stage growth behaviour, whereas in HVOF- and CGDS-CoNiCrAlY, the growth of TGOs proceeded in a parabolic manner.

Cracking appeared to proceed predominantly via discontinuity opening and crack propagation in the ceramic layer near the TC/BC interface. Power-law relationships between the maximum crack length and the TGO thickness were observed in all three CoNiCrAlYs; however, it appeared that the spray process had a strong influence on the power-law relationship.

Up to 1000 hours of thermal exposure, CGDS-CoNiCrAlY had a TGO growth behaviour and a cracking behaviour similar to HVOF-CoNiCrAlY, which results in better properties to those of the APS-CoNiCrAlY.

These results point to a potential advantage of using cold spray techniques to produce TBC bond coats for extending the life of TBC systems. The continuation of this work, in order to evaluate the longer term performance of the TBC system having the cold-sprayed bond coat, will provide further insight into the TGO growth mechanisms and rates and provide information on the durability of this system.

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