Oxidation Behaviour of CoNiCrAlY Bond Coats Produced by High Velocity Oxy-Fuel and Cold Gas Dynamic Sprayed Nitrogen Gas

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Abstract: The purpose of the current study was to investigate the microstructure and oxidation behavior of CoNiCrAlY coatings, deposited by the HVOF and CGDS techniques. The quality of the as-sprayed and oxidized bond coats was assessed in terms of their microstructure, especially porosity and oxide inclusion and mechanical properties, especially hardness. Sprayed samples were exposed to isothermal oxidation at 900 °C in air. Oxide growth rates were obtained from a series of mass gain measurements, while oxide scale compositions were determined using SEM, XRD and EDX analysis. Results obtained in this study show HVOF coating features high levels of visible defects, oxide content, spinel-type oxide and high oxide growth rate, whereas CGDS coatings show low oxide growth rate as a result of low porosity, oxide content and high hardness. The oxide scale on the CGDS coating after 1000 hrs of oxidation was composed of alumina and initiation of spinal type of oxides.

Keywords: Cold Gas Dynamic Spray (CGDS), High velocity oxygen-fuel (HVOF), bond coat

I. Introduction
Thermal barrier coatings (TBC) are used for gas turbine blades of power plants and aircraft engines for higher efficiency and long term durability. TBC system consists of MCrAlY bond coat and YSZ top coat. Bond coat enhances the adhesion of the ceramic top coat. Working conditions at elevated temperature lead to the oxidation of the bond coat which causes the formation of a thermally grown oxide (TGO) layer at the bond coat/top coat interface and continues to grow in thickness during thermal cycling by consuming the oxidation resistant element reservoir [1-3]. The oxidation resistance and the TGO quality depend, not only on the chemical composition but also on the technique used to produce the bond coat. CoNiCrAlY is typically coated by VPS (Vacuum plasma spraying), APS (Air-plasma spraying), LPPS (Low pressure plasma spraying) and HVOF (High velocity oxygen-fuel spraying) [4, 6]. The drawback of these techniques is that their inherent elevated temperature inevitably leads to changes in the coating microstructure namely oxide inclusions. APS gives a coating which has porosity and oxide impregnation. Shibata et al. [4] deposited CoNiCrAlY bond coat using APS, LPPS and HVOF and the extent of oxide contamination was 1.8, 0.16 and 0.94 wt. % respectively. F. Tang et al. [7] deposited CoNiCrAlY coating by HVOF and reported that in-process surface oxidation is detrimental to the TGO growth mechanism as it promotes the onset undesirable fast-growing nonalumina oxides that form protrusions and cause the TBC failure mechanisms. An alternative to above process is cold gas dynamic spray (CGDS) technique. In the CGDS spraying, the kinetic energy, rather than thermal energy is used to produce the bond coat [8-12]. In this process, the fine powders particles (5-42 μm dia) are propelled in a supersonic flow and get deposited on substrate after undergoing sever plastic deformation upon impacting the substrate. CGDS coating operates at lower temperatures and also uses inert gases such as helium and nitrogen which hinder oxidation and grain growth during deposition [13, 15]. Recent researches have showed the potential of CGDS compared to other VPS [23]. P. Richer et al. [16, 17] deposited CoNiCrAlY coating using CGDS sprayed with He gas reported that coating composed of alumina, without the presence of NiO or spinal-type mixed oxides. Q. Zhang et al. [18] studied oxidation behavior of NiCrAlY coatings deposited using CGDS technique. They reported the formation of (α-A₂O₃) at 900°C and 1000°C. The aim of the present work, therefore, is to compare the oxidation behavior of the bond coat material (CoNiCrAlY), applied using both techniques. The difference in the coating characteristics is expected due to the large difference in kinetic energy of deposition which in turn can modify the oxidation behavior of the coatings.

A. CoNiCrAlY powder characterization
Fig.1 shows XRD results of CoNiCrAlY powder, surface morphology and EDX analysis of elemental composition (wt. %) at selected points. This gas atomized powder has a spherical morphology and particle size range (10-42 μm dia.). The observed composition of the powder is in considerable agreement to that supplied by the supplier, except for a small difference in the concentration of yttrium. Since the γ phase is a solid solution of
Co, Ni, Cr etc. and has a higher mean atomic number, it appears brighter in BSE mode. Hence, the brighter phase is represented by $\gamma$ and the darker phase as $\beta$-NiAl/CoAl, which has a lower mean atomic number and hence lower contrast in BSE mode, as confirmed in references [16-20].

**Fig. 1** XRD pattern of CoNiCrAlY powder revealing a two-phases, $\gamma$+$\beta$ structure

**, Deposition techniques and equipment**

In cold spray process, the penning effect of incoming high velocity solid particles deforms the deposited material which tends to close any small pores or gaps in the underlying material [9, 11, 15 and 17]. In order to understand the effect of $N_2$ carrier gas was employed to carry and accelerate the CoNiCrAlY powder. The 316L stainless steel plates were cut into 300 x 300 x 2 mm size with a wheel cutter. Before the deposition, the plates were grit blasted with 20- grit alumina at a pressure of 0.3 MPa to increase surface roughness and ultrasonically cleaned in water and ethanol. Finally plates were cut into small pieces of (10 x 10 x 2 mm) size using wire electrical discharge machine for experiment. HVOF coating was carried out using HIPOJET-2700 model, using nitrogen as carrier gas.

**II. Results**

A. Characterization of as sprayed Coatings

1. As-sprayed HVOF coating

Fig. 2 (a, b, c) show the surface morphology, cross-sectional morphology and dendrites microstructure of as-sprayed HVOF coating. The microstructure of coating revealed semi-melted particles presented on the top of as-sprayed condition. The coating surface is rough in the as-sprayed condition due to the presence of melted and unmelted particles. The thicknesses of the coatings measured, is in the range 165-299μm. Coating shows, the dendrites are well packed and well interlocked to each other as shown in Fig. 2 (b). Fig. 2 (c) display relatively higher degree of porosity in HVOF coating.

**Fig. 2 SEM images of HVOF coating in as-sprayed condition**

2. CGDS with $N_2$ gas

Figure.3 (a) shows individual powder particles, not properly adhered to the surface, perhaps due to not acquiring the critical velocity required for the deposition. Hence, multi-impacts under $N_2$ carrier gas display relatively higher degree of porosity, portraying low carrying capability of accelerating gas (Fig 3 (b)). This behavior is due to the increase in density of the carrier gas ($N_2$ density is 1.2506 kg/m$^3$), and thereby reduced degree of plastic deformation of the spray particles is expected for the coating. Thus, higher porosity levels, larger splat size, and reduced plastic deformation degree was observed when compared to those of helium-processed coating [19, 20]. Fig.3 (c) shows the surface morphology of the coating, revealing pores and voids and the presence of higher splats attributing to the multi-impacts on the coated layer.
3. Nanoindentation analysis of the coatings
Table 1 show the nanoindentation measurements on coatings, CGDS sprayed with N₂ carrier gases and HVOF. A load of 11000 grams applied for 15 seconds and six indentations were made on each sample and the averages results were taken. The coating deposited by N₂ carrier gas was denser than that coated by HVOF. The deposition hardness is dependent on the velocities attained by the particle, and thereby the impact to cause plastic deformation on the surface. Hence, the impact velocity, being a function of the ratio of specific heats and inversely to the mass of carrier gas, improves the hardness with lower density and higher specific heat ratio of carrier gas. Hence, pure nitrogen displayed higher hardness in contrast to HVOF processing conditions for deposition coatings [21].

<table>
<thead>
<tr>
<th>Process</th>
<th>Load $P_{\text{max}}$ (mN)</th>
<th>Hardness (GPa)</th>
<th>Reduced modules $E_r$ (GPa)</th>
<th>Depth of penetration $H_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGDS N₂</td>
<td>11000</td>
<td>6.35</td>
<td>151.33</td>
<td>250</td>
</tr>
<tr>
<td>HVOF</td>
<td>11000</td>
<td>5.04</td>
<td>119.10</td>
<td>285</td>
</tr>
</tbody>
</table>

B. Characterization of oxidized scale
1. Oxidation Studies
1.1 Kinetics of HVOF and CGDS sprayed with N₂ coatings
The oxidation behavior of the coated stainless steel was investigated using discontinuous oxidation tests in air. The weight changes vs time plots for the oxidation of coatings in air at 900 °C are given in Fig. 4. The linear plots appear to follow parabolic kinetics. After 1000 hrs the parabolic rate constant, $K_p$ calculated using parabolic equation was found to be 1.28x$10^{-8}$ g/cm$^2$/s$^1$; for HVOF, 0.510x$10^{-8}$ g/cm$^2$/s$^1$; for N₂ gas, sprayed with CGDS [17-19, 22]. The results show that the CGDS sprayed with N₂ coated samples shows significant lower oxidation rate than the HVOF coated samples.

Fig. 4 Mass gain curve obtained during isothermal oxidation of the HVOF and CGDS sprayed with N₂ coatings after the oxidation at 900 °C for 1000 hrs

2 Characterization of Oxidized scale of CGDS sprayed with N₂
Fig. 5 shows the surface morphology of oxidized sample of CGDS sprayed with N₂ carrier gas coating oxidized at 900 °C for 200, 500 and 1000 hrs. The EDX analysis was done on oxidized surface was rich in Al, and O and small amount of Cr and Co. It is clear from XRD (Fig. 6) result that the intensity of the peaks associated to CoCr₂O₄ spinal-type oxides also increases, while the intensity of the α-Al₂O₃ peaks remains relatively low.

Fig. 5 Surface morphology of the CGDS coating sprayed with N₂ gas after the oxidation at 900 °C for different times

![Surface morphology of the CGDS coating sprayed with N₂ gas after the oxidation at 900 °C for different times](image)

XRD analysis carried out on the Feedstock powder was composed of γ and β-phases as depicted in Fig. 1. Fig. 6 shows XRD results for the oxides formed at various stages of oxidation. It is observed that the as-sprayed coating do not retain the typical two-phase microstructure (γ-matrix Co-Ni-Cr solid solution and β-NiAl/CoAl precipitates) initially found in the feedstock powder [16, 17]. The absence of β-phase in as-sprayed coating shows that transformations of microstructure have taken place during deposition. In CGDS coating, the absence of the β-phase is in accordance with findings [16].

Fig. 6 XRD patterns of oxidized CGDS coating sprayed with N₂ gas at the temperature of 900 °C for different times

![XRD patterns of oxidized CGDS coating sprayed with N₂ gas at the temperature of 900 °C for different times](image)

3 Characterization of Oxidized scale of HVOF

Figure 7 illustrates surface morphology of HVOF coating oxidized at 900 °C for 200, 500 and 1000 hrs for isothermal oxidation. Surface scale morphology of the oxidized coating it can be seen that the surface is mostly covered with an oxides scale composed of aluminum and oxygen having needle-like (or whisker-like, blade like) morphology which is characteristics of α-Al₂O₃, and NiO and spinal-type oxides. The EDX analysis was done on oxidized surface was rich in Co, Ni and O rich oxide. Figure 8 shows XRD pattern of coating reveal the existence of NiO oxides, α-Al₂O₃, and the γ solid solution. As suggested by F. Tang, P. Richer, and Saeidi et al. [7, 17, 23], “spinel” represent wither a mixture of some/all of other spinel mixed oxides such as NiCr₂O₄, NiAl₂O₄, CoAl₂O₄, CoCr₂O₄ and NiCo₂O₄, or a substitutional solid solution of (Ni, Co)(Al,Cr)₂O₄. From Fig. 8 for HVOF coating the surface morphology of the oxidized samples, it can be seen that the surface is the spinel-type oxides a mixture of α(Ni,Co)(Al,Cr)₂O₄, α-Al₂O₃ and also NiO. Oxide layer formed at 1000 hrs reveals the presence of an area with higher Ni concentration, which corresponds to an oxide on the coating surface with block-shape morphology is typical NiO, the presence of this oxide suggests that the coating is nearing the end of its Al-rich lifecycle. These findings are in accordance with those reported in study [7, 23, and 24].
Fig. 7 Oxide scale surface morphology of the HVOF coating after the oxidation at 900 °C for different times

Fig. 8 XRD patterns of oxidized HVOF coating at the temperature of 900 °C for different times

IV. Conclusions

- Cold-spray deposition of CoNiCrAlY powder using N₂ as carrier gas exhibited less dense morphological structure. This effect was attributed to the lower ratio of specific heats and high mass density of nitrogen as carrier gas.
- The oxide scale for the CGDS coating was predominantly composed of alumina, and initiation of growth of NiO or spinel-type mixed in thermally grown oxide layer.
- The oxide scale for the HVOF coating shows undesirable NiO and mixed spinel-type oxides during oxidation it suggests that the coating is nearing the end of its Al-rich lifecycle.

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References