Effect of surface conditions on internal oxidation and nitridation of HVOF MCrAlY coatings

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This study deals with the isothermal oxidation behaviour of high velocity oxy-fuel sprayed MCrAlY coatings. Both free-standing coatings and coatings attached to IN738 and CMSX4 substrates underwent isothermal oxidation at 1100°C for up to 100 h. The effect of surface conditions (as sprayed and polished) has been investigated. Scanning electron microscopy and energy dispersive X-ray analysis were used to characterise the details of oxidation behaviour. The results have shown that both surface conditions and substrate type have a pronounced effect on oxidation behaviour. Extensive internal oxidation and nitridation was observed for polished coatings on Inconel 738 and can be attributed to the combined effects of titanium diffusion from the substrate and enhanced surface diffusion due to polishing.

Keywords: HVOF, Surface conditions, Titanium diffusion, Internal oxidation

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Introduction

Thermal barrier coatings (TBCs)1,2 are used to protect turbine blades and similar components from the harsh conditions encountered in the hot gas stream. TBCs are layered structures, consisting of an outer, ceramic, layer which thermally insulates the underlying metallic component, and a metallic bond coat. As well as enhancing the adhesion of the ceramic top coat a key role of the bond coat is to provide corrosion and oxidation resistance. This is done by the generation of a protective thermally grown oxide (TGO), predominantly alumina, at the interface of the top coat and bond coat. The presence of the TGO is vital to the function of the TBC. However failure of TBCs is frequently associated with the TGO.3,4 Ideally a TGO forms rapidly but then grows very slowly.

To maintain a protective alumina TGO an aluminium reservoir is needed within the TBC. In MCrAlY bond coats, such as those considered in this paper, a two phase, γ/β, microstructure is frequently seen, with the β phase acting as an aluminium reservoir.5 It is known that the surface roughness can affect TGO growth, and that the initial TGO formed can go on to affect further TGO behaviour.6,7

Effects of substrate composition on the behaviour of coatings similar to those used in this work have previously been reported, with diffusion of titanium from the substrate being highlighted by several authors. Nickel et al.8 note that for NiCrAlY coatings, although low levels of Ti can improve scale adherence, for substrates with 3–4 wt-% diffusion of Ti through the coating can promote scale spallation. Tolpygo et al.9 show that the extent of oxidation induced rumpling of Pt-modified NiAl diffusion coatings depends on the Hf and C content of the underlying substrate, and note that Ti can buffer the solution of Hf in carbides. Ti is also listed as one of the surface contaminants which may be introduced by grit blasting and then lead to accelerated oxide growth, with a detrimental effect on coating lifetime.10 Duhamel et al.11 note that TBC adherence depends on the substrate, with Ti and Ta diffusing from the substrate, through the coating to the outer surface. This diffusion of Ti through the coating has also been reported by Pint and Unocic.12

This paper studies the effect of substrate and surface condition on the oxidation behaviour of high velocity oxy-fuel sprayed CoNiCrAlY coatings.

Experimental methods

All coatings included in this work were generated from a Co–31–7Ni–20–8Cr–8.1Al–0.5Y feedstock powder from Praxair (CO-210-24). This had a nominal size range of 45–20 µm and a chemically analysed oxygen content of 0.037 wt-%. Spraying was carried out using a Met Jet III liquid fuel HVOF gun. Full details of the spraying process and procedures are listed as HVOF2 in Ref. 13, and are very similar to the details given in Ref. 14, the only difference being that a N2 flowrate of 4.3 L min–1 was used for the current work.

The coatings were deposited onto substrates with approximate dimensions of 60 × 25 × 1.8 mm. Two different superalloy substrates were used: Inconel 738 and CMSX4, with compositions as given in Table 1.

Free-standing coatings were generated by spraying onto mild steel samples to a thickness of approximately
These coatings were then debonded from the mild steel by bending around a mandrel. The inclusion of free-standing coatings allowed the isolation of effects that were due to coating/substrate interactions. The as sprayed coatings had a surface roughness $R_a$ value of $6.1 \pm 0.2 \, \mu m$, for the polished coatings the $R_a$ decreased to $0.2 \pm 0.1 \, \mu m$.

Prior to oxidation all samples underwent a vacuum heat treatment for 2 h at 1100°C. Samples were exposed to air at 1100°C for times up to 100 h. Sample characterisation was carried out using an SEM equipped with energy dispersive X-ray spectroscopy.

### Table 1: Nominal compositions (wt-%) of substrates used in this work

|       | Ni | Cr | Co | Mo | Al | Ti | Ta | W | Zr | C   | B   | Nb | Hf | Re | La + Y |
|-------|----|----|----|----|----|----|----|----|----|-----|-----|----|----|----|--------|
| Inconel 738 | Bal | 16 | 8.5 | 1.7 | 3.5 | 3.5 | 1.7 | 25 | 0.05 | 0.09 | 0.10 | 2  |    |    |        |
| CMSX4   | Bal | 6.5 | 9   | 0.6 | 5.6 | 1   | 6.5 | 6  | 0.05 | 0.1  | 3   | 0.002 |    |    |    |

### Figures

1. Microstructure of as sprayed coated IN738 (top row) and coated CMSX4 (bottom row) after 100 h oxidation at 1100°C

2. β depletion zone thickness as function of oxidation time for as sprayed coatings

3. β depletion comparison of polished coatings as function of oxidation time
Results

For most samples β depletion zones were clearly seen to develop underneath an external oxide scale (Fig. 1). Measured β depletion zones as a function of oxidation time are shown in Figs. 2 and 3 for as sprayed and polished samples respectively. It can be seen that the depletion zones for as sprayed coatings on both substrates are very similar, and that both are notably greater than those observed for the free-standing coating (Fig. 2). For the polished coatings the measured β depletion zones for free-standing coatings and coatings on CMSX4 are all approximately twice as large as what was observed for the equivalent as sprayed...
coatings. EDS analysis of the β and γ phases in the as sprayed coatings after 100 h oxidation showed the presence of titanium in the coating on Inconel 738: ~0.6 wt-% was found in the γ phase and ~0.2 wt-% was found in the β phase. EDS results could not confirm the presence of Ti in the 100 h oxidised coating on the CMSX4 substrate. No results for Inconel 738 are included in Fig. 3 because it was not possible to make meaningful measurements of any β depletion zone due to the extensive internal oxidation attack seen in Fig. 4. Additional phases are seen to have formed in the near surface region. The depth to which these phases extend increases with the oxidation time. This type of internal attack was only observed for the polished coatings on Inconel 738 substrates.

Results from additional, shorter term, oxidation experiments are shown in Fig. 5 where the samples have been exposed for only 2 h but the same attack is already seen to have started.

6 EDS mapping of near surface region of polished IN738 after 2 h exposure at 1100°C
EDS mapping (Fig. 6) reveals that the phases formed are enriched in Al, O and N, with the EDS maps and compositions (Table 2) being consistent with the outermost region containing alumina and the region below that containing Al rich nitrides.

For the polished coatings on Inconel 738 a third phase was noted within the coating near the coating/substrate interface after 100 h oxidation (Fig. 7). EDS analysis of the phase was consistent with it being TiN (Table 3).

Discussion

An increased extent of β depletion is seen for all attached coatings compared to the free-standing coatings (Figs. 2 and 3). It is well known that thermal sprayed coatings contain residual stresses. On impact any molten regions of the particles solidify and then the splat cools and contracts, however the attachment to the underlying coating layers and substrate constrains this contraction.15,16 This tensile quenching stress is combined with the thermal mis-match stress, caused due to differential thermal contraction of coating and substrate, to produce the overall residual stress distribution which can be tensile or compressive.16 Metejicek et al.16 and Santana et al.17 respectively report tensile residual stresses in plasma sprayed NiCrAlY and HVOF nickel based coatings on steel. Itoh et al. highlight that in HVOF coatings a peening effect can reduce the magnitude of residual stresses.18 While it must be noted that the current work does not included any direct measurement of residual stresses for the coatings used here, based on the results in the open literature we have assumed the presence of a tensile residual stress. Detachment from the substrate would then be expected to relieve the majority of the tensile stresses. So this means that the stress states in the free-standing and attached coatings will be different. It is suggested that the tensile stresses in the attached coatings enhance diffusion rates, thereby resulting in the observed larger depletion regions for the attached coatings compared to the free-standing coatings.

For the coatings on CMSX4 substrates it is seen that the polished coatings have smaller β depletion zones than the as sprayed coatings. This can at least partially be attributed to the increased roughness, and correspondingly larger real surface area, of the as sprayed coatings.

It is clear that the polished coatings on Inconel 738 behave very differently to all other samples. Extensive internal oxidation occurs for these coatings. This was not seen for the same type of coatings on the same substrate in the as-sprayed rather than polished condition. In addition to changing the surface roughness polishing introduces mechanical work to the surface and can thereby increase the dislocation density. Dislocations are known to act as fast diffusion paths. Polishing can therefore enhance diffusion in the surface and near surface regions. This enhanced diffusion is thought to be a contributing factor to the internal oxidation seen in the polished coatings on Inconel 738.

The polished coatings on CMSX4 were prepared in the same way so would have also undergone the same enhancement in diffusion however no internal oxidation or nitridation was seen for those coatings. The difference between these two cases is the substrate. EDS results proved that titanium from the Inconel 738 substrate diffused into the coating. Titanium is of particular interest as it has been previously reported to be able to rapidly diffuse to form TiO at a coating surface beneath the alumina scale.19 CMSX4 has a significantly lower titanium content than Inconel 738, hence no titanium diffusion was expected, or observed, for coatings on CMSX4.

It is suggested that the observed extensive internal oxidation and nitridation of the polished samples on Inconel 738 is due to the combination of two factors: the enhanced diffusion due to increased dislocation density resulting from polishing and the presence of titanium. The absence of internal oxidation and nitridation in both the as-sprayed coatings on Inconel 738 and the polished coatings on CMSX4 supports the proposition that both enhanced surface diffusion and the presence of titanium are required for the observed effects to occur.

The precise role of titanium requires further study. It seems that the presence of titanium, combined with fast inward diffusion routes for oxygen and nitrogen prevent a protective alumina film from forming. It is possible

| Table 2 | EDS analysis of composition of aluminium nitrides/wt-% |
|--------|------------------|
| Co     | 1.5±0.3          |
| Ni     | 1.6±0.8          |
| Cr     | 1.0±0.5          |
| Al     | 62.3±0.3         |
| N      | 33.6±0.7         |
| Co     | 0.6±0.2          |
| Ni     | 0.6±0.3          |
| Cr     | 0.4±0.2          |
| Al     | 49.6±1.3         |
| N      | 48.6±16          |

| Table 3 | EDS analysis of composition of titanium nitrides |
|--------|-----------------------------------------------|
| TiN    | Co    | Ni    | Cr    | Al     | N      | Ti     |
| wt-%   | 12.7±2.4 | 16.5±2.8 | 9.4±1.3 | <1     | 45.7±3.2 |
| at-%   | 7.4±0.6  | 9.8±1.7  | 6.5±0.8 | <1     | 33.4±3.9 |

Materials at High Temperatures 2015 VOL 32 NO 1–2 219
that TiO forms within the coating, promoting nucleation of internal alumina. Once this internal oxidation, and nitridation, starts it continues, assisted and even accelerated by the volume expansion upon reaction.20 However, it should be noted that no TiO was detected in this work and more detailed study is required to elucidate the precise mechanisms at work.

Conclusions

The work presented in this paper has shown that as follows:

1. More extensive β depletion occurred during oxidation of coatings attached to superalloy substrates compared to free-standing coatings. It is proposed that this is due to enhanced diffusion in attached coatings resulting from tensile residual stresses.

2. For attached and free-standing coatings, a larger surface roughness produces more extensive β depletion zones.

3. For polished coatings on the Inconel 738 substrate, with an enhanced level of Ti compared to CMSX4, extensive internal oxidation and nitridation occurs during oxidation. This is attributed to the combined effects of enhanced surface diffusion and the presence of titanium.

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