Effect of Bondcoat Thickness on High Temperature Hot Corrosion of $\text{ZrO}_2\text{-}8\text{Y}_2\text{O}_3$ Thermal Barrier Coating

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Thermal barrier coatings (TBCs) are widely used for industrial and aero turbines. The use of residual fuel oil is well known due to economic reasons, which causes hot corrosion. Hot corrosion over extended exposures reduces durability. Therefore, there is a requirement to develop new design approaches for TBCs in order to operate under hot corrosion environment. In this paper, the effect of bond coat thickness on the hot corrosion resistance was studied. Hot corrosion test were carried out in 50 wt.% Na_2SO_4 + 50 wt.% V_2O_5 molten salt at 950 °C for 50 hours. The characterizations of the coatings included X-ray diffraction analysis, scanning electron microscopy and optical microscope. Results indicated that TBCs with thick bond coat exhibited superior hot corrosion resistance to the TBCs with conventional bond coat.

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1. Introduction

Thermal barrier coatings (TBCs) are generally used in jet engines and land-based turbines as insulating layers to protect the underlying components from the high temperatures. Typical TBCs have a two-layered structure consisting of an oxidation protective bondcoat and thermally insulating yttria stabilized zirconia (YSZ) topcoat [1–3]. Bondcoat is important for adhesion and grading the thermal expansion mismatch between the top and substrate. A typical bond coat contains Ni, Cr, Al, and Y, with Ni as the primary element for nickel-alloy substrate application [4]. A third layer present in a TBC is the Thermally Grown Oxide (TGO). This layer forms during TBC deposition and engine operation [4–5]. For industrial turbine engines or diesel engines burning low quality fuel due to economic reasons causes hot corrosion at approximately 700–900 °C. Low-quality fuels usually contain Impurities such as Na and V which can form Na_2SO_4 and V_2O_5 salt on the surface of component. Such fused salt caused hot corrosion and leaded cracking and spalling of TBCs [6, 7]. The life of bond coat is limited due to oxidation/corrosion and inter-diffusion between the substrate and bond coatings. Due to high quality performance of these coatings for variety of super alloys for over two decades in different applications, MCrAlY coatings were studied extensively [8]. Significant amount of work was carried out in developing the hot corrosion resistant MCrAlY bond coatings [8, 9].

In the present investigation, effect of bond coat thickness was studied for improving oxidation and hot corrosion resistance.

2. Experimental

Udmet-720 (wt. %: Co = 14.7, Cr = 17.9, Mo = 3.0, W = 1.3, Ti = 5.0, Al = 2.5, C = 0.03, Ni = balance) substrates with nominal dimensions of $25 \times 25 \times 2 \text{ mm}^3$ were utilized for the experimentation. The samples were cut from a sheet and sand-blasting was performed using alumina particles bombardment at right-angle to the surface. Surface roughness (Ra) of the substrates was found to be in the range of 3–3.5 μm . The freshly blasted surfaces were immediately held in a chuck, which was later rotated at an optimized speed of 120 rpm. Plasma spraying was performed, using 9 MB Sulzer Metco gun, to deposit both topcoat and two types of bondcoats having different thickness (thin $\approx 90 \mu\text{m}$ and thick $\approx 250 \mu\text{m}$). The spray angle was maintained as $\approx 90^\circ\text{C}$. During the spraying process the gun was moved to and fro at the speed of 12 meter/minute. Substrate's temperature was maintained at $\approx 200^\circ\text{C}$ using a constant flow of compressed air during the coating process. Important spraying variables parameters for the topcoat and bondcoat are given in Table I. Details of the powders are given in Table II. As-sprayed coated samples were exposed to hot corrosion testing. A mixture of 50% V_2O_5 and 50% Na_2SO_4 was spread over the samples with a concentration of 30 mg/cm^2 as per procedure mentioned in [9]. The samples were placed in a furnace and heated up to temperature 950 °C. The samples were exposed to hot corrosion testing for a total duration of 50 hours.

3. Results and discussion

3.1. Surface observations

The surface of the topcoat of sprayed sample showed splot of YSZ, some unmelted and semimelted particles while after exposure of 50 hours to hot corrosion environment, many rod like and agglomerated crystals were

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TABLE I

Parameters of plasma spraying machine for bondcoat and topcoat.

parameters	spraying powder	
	CoNiCrAlY (bondcoat)	YSZ (topcoat)
current [A]	600	600
voltage [V]	66	66
primary gas, Ar [SLPM]	55	32
secondary gas, H ₂ [SLPM]	8	10
powder feed rate [g/min]	150	150
spray distance [mm]	110	110

TABLE II

Chemical Compositions, morphology and particle size of powders for topcoat and bondcoat.

powder	chemistry	particle	
		size	morphology
Metco-204B (topcoat)	Zr stabilized with 8% Y	45 to 75 μm	Spherical
AMDRY-955C (bondcoat)	Co32-Ni21- Cr8-Al0.5-Y	45 to 75 μm	spherical

observed on the surface, Fig. 1. EDS analysis of these agglomerates and rod like structure revealed ZrO_2 and YVO_4 respectively. It seemed that the degradation of topcoat started by the formation of YVO_4 crystals. Some of these crystal rods demonstrated to be placed on the surface while others were firmly adhered to the topcoat, Fig. 1. During exposure of salt mixture i.e. 50% Na_2SO_4 and 50% V_2O_5 reacted with each other and formed a eutectic compound Na_2VO_3 .

The formation of Na_2VO_3 acted a corrosion catalyst and served as an oxygen carrier. Na_2VO_3 entered into the crevices and pores, present within the plasma sprayed coatings, reacted vigorously with Y_2O_3 , added in the pure zirconia solid solution for stabilizing the tetragonal crystal structure. The resultant reactant yielded YVO_4 [9].

Fig. 1. SEM micrographs showing surface morphology of samples (a) as sprayed and (b) after 50 hours exposure to hot corrosion environment.

3.2. Cross sectional observations

After 50 hours exposure at 950 °C in hot corrosion environment, cross sectional of samples revealed that sample with thin bondcoat (S1) had thicker thermally grown oxide (TGO) as compared to sample with thick bondcoat (S2), Fig. 2. Further, it was noted that cracks started to appear in sample S1, Fig. 2. In order to understand the cracking phenomenon at the interface of bondcoat and topcoat, a detailed analysis of the cross sections were given. The cross section of the sample revealed different features, Fig. 3. EDS analysis showed that each feature had its own distinct chemical composition. The chemical composition (in % atomic) of these features is presented in Table III. In order to confirm the formation of different phases, the topcoat was delaminated by chemical etching process. For this purpose 50% diluted HCl was used which attacked the interface of both bondcoat-topcoat and substrate-bondcoat. As a result, a delaminated topcoat was obtained with attached phases, formed during the hot corrosion. The delaminated topcoat was washed with water and used for XRD. From the XRD analysis it revealed that the formation of spinels consists of NiCr_2O_4 and CoCr_2O_4 along with perovskite structure of NiCrO_3 at the interface of bondcoat and the topcoat, Fig. 4. Development of these structures caused volumetric changes and forced to crack the interface. Samples, after 50 hours hot corrosion testing, demonstrated that overall oxidation condition of bondcoat was more severe in sample S1 as compared to the sample S2, Fig. 5. EDS analysis at the boundaries of the splats showed that no “vanadium” is present in sample S2, whereas, sample S1 revealed “vanadium” in analysis, Fig. 6, this demonstrates that vanadium oxide crossed the diffusion barrier of alumina in case of sample S1 due to presence of cracks. This may be due to inter-diffusion between the bond coat and the underlying superalloy because minor alloy additions (S, Ta and W) lead to an increase in the growth rate of the TGO layer and promoted the formation of non-protective oxide scale [10] because this sample with thin bondcoat was more affected.

TABLE III

Chemical composition of different phases marked in Fig. 3 (exposed for 50 hours at 950 °C).

location	% age, atomic				possible phase
	Al	Cr	Co	Ni	
1	9	20	35	36	CoNiO_3
2	43	35	11	10	AlCrO_3
3	38	46	9	7	
4	49	14	19	17	Al_2O_3
5	6	23	37	34	CoNiO_3

4. Conclusion

The coatings were exposed to hot corrosion using corrosive salts of Na_2SO_4 and V_2O_5 . The results demonstrated that the Y_2O_3 present in solid solution of ZrO_2

Fig. 2. SEM micrographs after 50 hours exposure to hot corrosion environment showing, cross section of samples (a) S2 with thin TGO and (b) S1 with thick TGO and cracks (arrows).

Fig. 3. SEM micrograph showing discrete sites at the interface in a sample exposed for 50 hours showing different features (Sites-1 and 5). Sites-1 to 5 represent locations for EDS analyses reported in Table III.

reacted with the salt mixture and formed rods of yttrium vanadate (YVO_4). Reaction of oxygen with various metallic elements in the bondcoat resulted in formation of spinels consisting of NiCr_2O_4 and CoCr_2O_4 along with perovskite structure of NiCrO_3 at the interface of bondcoat and the topcoat. Development of these structures forced to crack the interface. Due to formation of thick TGO and inter-diffusion between the bondcoat and

Fig. 4. XRD pattern showing different phases formed in the delaminated coating of S1 sample exposed at 950 °C for 50 hours.

Fig. 5. Samples exposed at 950 °C for 50 hours, indicating more oxidation in (b) S1 with thin bondcoat as compared to (a) S2 with thick bondcoat.

Fig. 6. Samples exposed at 950 °C for 50 hours, EDS analysis at the boundaries of the splats showed that no “vanadium” is present in (a) sample S2, whereas, (b) sample S1 revealed “vanadium” in analysis.

the underlying superalloy, the sample with thin bondcoat showed low resistance against spalling as compared to the sample with thick bondcoat.

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