Structure and durability evaluation of YSZ + Al₂O₃ composite TBCs with APS and HVOF bond coats under thermal cycling conditions

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Abstract

Plasma sprayed thermal barrier coatings (TBCs) are applied to gas turbine components for providing thermal insulation and oxidation resistance. The TBC systems currently in use on superalloy substrates typically consist of a metallic MCrAlY-based bond coat and an insulating Y₂O₃ partially stabilized ZrO₂ (YSZ) as a ceramic top coat (ZrO₂ 7–8 wt.% Y₂O₃). The oxidation of bond coat underlying yttria-stabilized zirconia (YSZ) is a significant factor in controlling the failure of TBCs. The oxidation of bond coat induces to the formation of a thermally grown oxide (TGO) layer at the bond coat/YSZ interface. The thickening of the TGO layer increases the stresses and leads to the spallation of TBCs. If the TGO were composed of a continuous scale of Al₂O₃, it would act as a diffusion barrier to suppress the formation of other detrimental mixed oxides during the extended thermal exposure in service, thus helping to protect the substrate from further oxidation and improving the durability. The TBC layers are usually coated onto the superalloy substrate using the APS (Atmospheric plasma spray) process because of economic and practical considerations. As well as, HVOF (High velocity oxygen fuel) bond coat provides a good microstructure and better adhesion compared with the APS process. Therefore, there is a need to understand the cycling oxidation characteristic and failure mode in TBC systems having bond coat prepared using different processes. In the present investigation, the growth of TGO layers was studied to evaluate the cyclic oxidation behavior of YSZ/Al₂O₃ composite TBC systems with APS-NiCrAlY and HVOF-NiCrAlY bond coats. Interface morphology is significantly effective factor in occurrence of the oxide layer. Oxide layer thickening rate is slower in APS bond coated TBCs than HVOF bond coated systems under thermal cycle conditions at 1200 °C. The YSZ/Al₂O₃ particle composite systems with APS bond coat have a higher thermal cycle life time than with the HVOF bond coating.

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1. Introduction

Plasma sprayed thermal barrier coatings (TBCs) are applied to hot section parts in both aero and stationary gas turbine engines for providing thermal protection. A typical TBC system includes a MCrAlY bond coat (M: Ni and/or Co) as oxidation resistant layer and yttria stabilized zirconia (YSZ) as thermal insulation layer, because of its low thermal conductivity. The top insulative ceramic layer reduces the temperature of the underlying superalloy in relation to the gas path temperature. The bond coat helps to provide higher oxidation resistance to the superalloy and reduces also the thermal expansion mismatch between the ceramic TBC and the superalloy [1–3]. When exposed to high temperatures, oxidation of the bond coat results in the formation of a thermally grown oxide (TGO) layer at the ceramic/bond coat interface. TGO layer generally includes predominantly alumina (Al₂O₃) and also complex oxides as Cr₂O₃, NiO, and (Ni, Co) (Cr, Al)₂O₆. The high coverage of the mixed oxide on the interface leads to the early spalling of the TBC. A uniform and dense Al₂O₃ scale is desirable for low growth rate of TGO layer. The thickness and composition of the TGO layer determine the durability of TBC under thermal cycle conditions. As a result of increase in thickness of the TGO, internal stress increases and leads to spallation failure of TBC. The growth rate of the oxide scales on bond coatings can be influenced by variations of the exposure temperature, hold time, top coating composition and thickness, bond coat surface roughness and spray methods [4–9]. The addition of Al₂O₃ into YSZ improves the thermo-mechanical properties of TBC and reduces the thermal expansion mismatch between bond coat and top coat. The use of alumina particles into YSZ coating can decrease oxygen diffusivity through this layer. Al₂O₃ is not soluble within ZrO₂ and forms a rigid matrix around the ZrO₂ particles which causes a local compressive stress and hinders the phase transformation of zirconia. Therefore the growth of TGO thickness is suppressed by alumina addition [10–15]. In order to determine the thermal cycling lifetime and oxidation behavior of TBCs during high-temperature cycling at 1200 °C, in this study, the bond coats were deposited by APS and HVOF methods. The relationship...
between the oxidation properties and the interface damage is discussed, and the advantages of the HVOF and APS processes for forming a bond coat in the cyclic conditions are explained.

2. Experimental

2.1. Material and methods

Inconel 718 nickel based superalloy disk shaped samples with a diameter of 25.4 mm and thicknesses of 4 mm, were used as substrate. Prior to deposition, the substrate was grit blasted using corundum, in order to remove surface oxides and to improve its adhesive strength. The surface roughness of the substrates was measured as 3.6 μm after a grit blasting, followed by ultrasonic cleaning with acetone. Commercial Metco Amdry 962 (Ni–22Cr–10Al–1Y) and Amdry 9951 (Co–32Ni–21Cr–8Al–0.5Y) powders were selected to manufacture the bond coats and 65 wt.% Metco 204NS (ZrO₂–8 wt.%Y₂O₃) + 35 wt.% Metco 101NS(Al₂O₃) mixed powders used for top coat (Fig. 1). Blending of powders is performed in Turbula for 2 h. Particle size distribution evaluated by laser particle size analyzer. The powder mixture exhibits a nominal particle size distribution varying from 25 μm to 95 μm. The spray torches (APS and HVOF gun) were mounted on a commercial six-axis ABB robot that was capable of linear traversing speeds of up to 1000 mm/s. Plasma spraying was performed by means of F4 gun from Sulzer Metco and a plasma jet power in the range of 40–50 kW. In the case of HVOF coatings, the torch used was a gas fuelled HVOF gun (DJ2600). The powder injection was radial and the gas flow was obtained by the combustion between oxygen and hydrogen in HVOF process. Both process parameters are shown in Table 1. During spraying the substrate was continuously cooled from the backside via an air cooling nozzle. The substrate temperature was continuously recorded by a thermocouple inserted into the center.

In order to evaluate and compare the durability of the various TBC systems, laboratory thermal cycle testing was conducted in a programmable, automated test unit. For each condition, at least three samples were subjected to the following thermal cycling condition; 6 min heating at 1200 °C, 2 min cooling. The lifetime of the coatings was defined by the number of cycles at which 50% of total coating surface area is spalled or delaminated. The microstructures of as sprayed and thermally cycled coatings were investigated by scanning electron microscopy (SEM, JEOL 6060). The constituent phases of the TBCs were analyzed by X-ray diffractometry (Rigaku Dmax 2200 PC). In order to quantitatively determine the level of porosity, an optical microscope equipped with an image analyzer (Nih Image-J 1.43U software) was used.

![Image 1](Fig. 1. Powder mixture (ZrO₂–8 wt.%Y₂O₃ + (99.95% purity) Al₂O₃) for composite coating.)

### Table 1

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<tr>
<th>Deposition parameters for the thermal sprayed APS and HVOF bond coatings and APS top coatings.</th>
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<tr>
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<td><strong>HVOF bond coatings</strong></td>
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3. Results and discussions

3.1. Microstructural characterizations of the coatings

The top surface morphology and the chemical composition of the as-sprayed samples were examined by scanning electron microscopy (SEM) and EDX analysis. Dark regions on top surface (seen in Fig. 2a,c) are analyzed as Al₂O₃ and remained gray coloured regions are YSZ. Portosity levels of the top coatings were measured as 6–10% by image analysis software. Fig. 2b and d shows the cross section of the as-sprayed YSZ + Al₂O₃ top coatings on MCrAlY based bond coats which are produced by APS and HVOF processes. All of the top coatings showed the lamellar structure which is the characteristic of plasma sprayed depositions. The thickness of the ceramic top coat and bond coats was measured as 200–240 μm and 120–170 μm, respectively.

The oxidation of bond coat at high temperatures produces a thermally grown oxide (TGO) layer located between bond coat and top coat. A TGO layer is formed on the bond coat surface due to the oxygen penetration through the porosity of the ceramic layer. Thickness of this layer increases with increasing oxidation time and temperature. In addition oxygen penetrated through interlamellar of bond coat so oxide regions formed within a bond layer. Ni and Cr show no changes in concentration after thermal cycling while concentration of Al and O increased at the interface which indicates the presence of Al₂O₃. Some mixed oxides and their clusters are formed at around TGO layer. The formation of these clusters is attributed to the localized low aluminum concentration at the ceramic/TGO interface. As shown in Fig. 3a crack formation occurred at the TGO/YSZ interface. The TGO usually comprises large residual compressive stresses when it cools to ambient temperature, because of its thermal expansion mismatch with superalloy substrate. During the thermal cycling, the stress relieving occurs which is accompanied with tensile stresses parallel to TGO/ceramic layer interface that leads to crack and delamination crack at interface [10–13]. Al₂O₃ particles within the ceramic layer work as diffusion barrier, however TGO thickening is limited during longtime oxidation. The TGO thickness varies between 1 μm and 3 μm. TGO thicknesses are thicker (>4 μm) without Al₂O₃ particle in YSZ based coatings.

It is implied that the concentration and distribution of Ni and Cr show no substantial changes before and after they are thermally cycled, whereas the concentration of O and Al increased at the interface of bond coat/top coat or in some areas within the bond coat after oxidation which reveals the presence of Al₂O₃ in this zones. Continuous scaled Al₂O₃ performed as diffusion barrier to suppress the formation of other detrimental complex oxide compounds. TGO thickening will have a significant impact on the durability of the TBC system, as excessive TGO growth can certainly increase the stress build-up between the ceramic and bond coat, leading to TBC delamination [6]. The APS-bond coat shows an oxide layer of dominantly Al₂O₃ formed after thermal cycling, along with some mixed oxide clusters between this oxide layer and the ceramic top
coat. The mixed oxide clusters were comprised of nickel oxide, chromia, spinel (Fig. 3b). HVOF-bond coat also consists of an Al$_2$O$_3$ layer and less mixed oxide clusters. After extended thermal cycling, however, irregular crack formation occurred and the coalescence of the porosity led to cracking instantly above the bond coat. The TGO thicknesses were measured to 8–10 μm for APS-bond coated systems and 6–8 μm for HVOF-bond coated systems. The addition of Al$_2$O$_3$ improved the sintering resistance of the YSZ coatings[16].

3.2. XRD analysis

Fig. 4 shows XRD patterns of plasma sprayed composite YSZ coatings as-sprayed and after thermal cycling test. The as-sprayed coating is mainly composed of t-ZrO$_2$, little Al$_2$O$_3$ phases. After thermal cycling test the amount of Al$_2$O$_3$ phases increased and an Al$_{1+x}$Zr$_{1-y}$ based phase is formed. According to the phase diagram, the Al$_2$O$_3$ reacts with Y$_2$O$_3$ at the high temperature but needs a long time. Plasma spraying is such a rapid cooling process that the elements cannot be diffused[17, 18]. No phase transformation was observed after test.

3.3. Thermal cycle life of coatings

TBC systems have a tendency to fail by spalling or by debonding processes under cyclic high-temperature conditions. The growth of the TGO between the bond coat and the top coat layers causes great internal stresses, which lead to the spallation of TBC. The first
damages occurred at the extreme edges of the coatings. The severe heating and cooling led to stress concentration at the edges (Fig. 5a and c). When a single crack appeared, stress fields increased and rapid cracking progresses. Then macrocrack propagation occurs. Fig. 5 presents failure modes of the coatings at 1200 °C under thermal cycling conditions. For both coating systems totally 8 thermal cycle test samples were used. Until 300 thermal cycles, the composite YSZ + \( \text{Al}_2\text{O}_3 \) top coat with APS bond coatings (APS BC/APS TC) kept their integrity without spallation. After 305 thermal cycles, spallation started at the edges of the top coatings. Buckling of top coat started after 312 thermal cycles (Fig. 5a). As a result of the thermal expansion mismatch stresses, buckling started. After the 552 thermal cycles, top coat spallation reached critical level, and spallation region measured as 35% of top surface layer (Fig. 5b). Additionally, edge chipping was observed after 305 thermal cycles on the HVOF BC/APS TC system (Fig. 5c). Likewise, top coat (HVOF-BC) spalled after 451 thermal cycles (Fig. 5d).

Top coats were separated with cracking from the bond coat surface. Thus, interface roughness between bond coat and top coat plays an important role on durability during thermal cycling at elevated temperatures. In the case of APS bond coat surface roughness was higher than HVOF BC and higher surface roughness of the bond coat led to higher mechanical locking between top coat and bond coat. Adhesion properties of rough bond coat surface improved thermal cycle lifetime of top coat and smooth HVOF-BC surface reduced the adhesion of top coat. Results of the study showed that TGO thickening rate of HVOF BC system was faster than the APS BC and adhesion reduced at interface area with the TGO formation. The presence of local chemical changes in TGO composition increased the interior stress and led to cracking during thermal cycle test. Similarly, thickness of TGO increased the stress locally and caused the formation of micro-cracks at the interface TGO/top coat. The thermal cycle lifetime of the \( \text{Al}_2\text{O}_3 + \text{YSZ} \) composite coating is much higher than that of traditional YSZ coating. In order to determine the best fitting probability distributions, Minotab software was used. Weibull was selected as the best fitting distribution given that the AD (Anderson–Darling) statistic of Weibull is the smallest number even though the corresponding P-value is less than 0.1. Damage progression is often by micro-cracking extension followed by linking-up and then large crack propagation, as observed also previously [19]. The presence of cracks at the interface TGO/top coat and the rumpling effect are due to the residual stress accumulated during thermal cycle tests.

4. Conclusions

Although the APS method is considered as an economic process for producing TBCs, it comprises high porosity and causes the oxygen penetration toward the bond coat which is accompanied with TGO growth and internal oxidation of MCrAlY layer. During cycling of TBCs, the TGO layer was formed along the interface of the bond coat and ceramic layer which includes mainly mixed oxides. The presence of TGO discontinuities could increase the internal stress locally and thus cause the formation of micro-cracks at the interface TGO/top coat. The delamination crack occurred when the microcracks linked up and macro-crack propagation occurred in the presence of the internal stress. Although internal oxidation of the bond coat was severe for top

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**Fig. 4.** XRD patterns of the TBCs.

**Fig. 5.** Macroviews of the TBCs after thermal cycles: (a) APS BC/APS TC after 312 cycles, (b) APS BC/APS TC after 550 cycles, (c) HVOF BC/HVOF TC after 305 cycles, (d) HVOF BC/HVOF TC after 450 cycles, (e) failure probability plots for thermal cycle lifetimes.
coatings, it decreased substantially for the bond coat of YSZ + Al₂O₃ coating due to lower oxygen ingress. The results show that adding alumina (35 wt.%) into the YSZ is effective in improving the thermal cycle life time of YSZ (yttria stabilized zirconia) thermal barrier coatings. However crack propagation during thermal cycling appears to be controlled by TGO growth. Alumina particle composited top coatings tend to have a low oxygen diffusion. This is helpful to limit thermal grown oxide on bond coat and improve the thermal cycle life time and mechanical properties of YSZ top coat at 1200 °C. Thermal cycle life time of the HVOF–BC system lower than APS–BC. APS–BC has a higher adherence to top coat.

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References