

Failure Mechanisms for Zirconia Based Thermal Barrier Coatings

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Failure mechanisms were investigated for the two layer thermal barrier coatings consisting of NiCrAlY bond coat and ZrO_2 -8wt.% Y_2O_3 ceramic coating during cyclic oxidation. Al_2O_3 developed at the ceramic coating/bond coat interface first, followed by the Cr/Ni rich oxides such as $NiCr_2O_4$ and $Ni(Al, Cr)_2O_4$ during cyclic oxidation. It was observed that the spalling of ceramic coatings took place primarily within the NiCrAlY bond coat oxidation products or at the interface between the bond coat oxidation products and zirconia based ceramic coating or the bond coat. It was also observed that the fracture within these oxidation products occurred with the formation of $Ni(Cr, Al)_2O_4$ spinel or Cr/Ni rich oxides. It was therefore concluded that the formation of these oxides was a life-limiting event for the thermal barrier coatings.

Key words : Thermal barrier coatings, Electron beam-physical vapor deposition, Plasma thermal spray, Zirconia

I. Introduction

Insulating ceramic coatings known as thermal barrier coatings (TBCs) are currently being used for the hot section components in gas turbine and diesel engines to improve performance and efficiency.¹⁻³⁾ The generally accepted TBC system used for gas turbine engines has a duplex structure which consists of a ZrO_2 based ceramic (containing stabilizing oxides such as Y_2O_3 , CeO_2 or MgO) coating on a bond coat of MCrAlY (M=Ni or/and Co) alloy.⁴⁻⁶⁾ The application of two layer TBCs to the hot section component metals in heat engines is primarily accomplished by plasma thermal spray or electron beam-physical vapor deposition (EB-PVD). The potential benefits of TBCs include higher turbine inlet temperature, lower metal temperature, reduced cooling air flow and extended life of the metal component.^{7,8)} The selection of a deposition technique would depend on the component geometry, service conditions and combustion environment.^{9,10)}

Desirable properties of the ceramic thermal barrier coating include a high thermal expansion coefficient, low thermal conductivity, chemical stability in the combustion environment and thermal shock resistance.^{11,12)} The most durable ceramic materials used for the TBC in a cyclic high temperature environment were found to be formed from the partially stabilized zirconia (psz) compositions (ZrO_2 with 6 to 8 wt.% Y_2O_3).^{11,12)}

The major difficulty in use of a TBC on a superalloy substrate in a cyclic high temperature environment is spalling of the ceramic coating. It is believed that spallation of the ceramic coating is caused by the stresses generated during cyclic oxidation. The source of stresses that lead to the spallation includes: the thermal expansion mismatch between the ceramic and the metal, the tem-

perature gradient across the ceramic and the metal, phase transformations of psz ceramic and the bond coat oxidation.¹³⁻¹⁵⁾ Other factors which may play a role include bond coat deformation and ceramic sintering shrinkage.¹³⁻¹⁵⁾ Among the factors, bond coat oxidation appears to influence strongly TBC failure.⁴⁻⁶⁾ It is considered that the bond coat is oxidized by two mechanisms during cyclic oxidation. One is ionic diffusion through the lattice and the other is gaseous transport along the interconnected cracks and pores existing in the psz coating. Upon high temperature exposure of TBCs, the oxidation products of the metallic bond coat form at the interface between the ceramic coating and the bond coat. These oxidation products have a structure and composition different from the ceramic coating as well as the bond coat, suggesting that their thermal and mechanical properties differ from the ceramic and the metal. The formation of the oxidation products at the interface would lead to the spallation of the ceramic coating by the fracture within the oxidation products. Thus, characterization of the oxidation products formed at the psz ceramic/bond coat interface should provide an improved understanding of TBC failure. Few investigations have included a detailed analysis of the reaction products developed at the psz ceramic/NiCrAlY bond coat.^{16,17)} In this study, the diffusional reaction products developed at the interface between psz ceramic coating and NiCrAlY bond coat during cyclic oxidation were characterized. In addition, the TBC failure mechanisms due to the bond coat oxidation were investigated.

II. Experimental Procedure

Disk-shaped(25 mm diameter by 3 mm thick) nickel

based superalloy (Rene'N4) specimens were prepared for two-layer thermal barrier coatings. The TBCs were deposited by either EB-PVD or plasma thermal spray. The compositions of ceramic and metallic bond coat used for the TBCs were ZrO_2 -8 wt.% Y_2O_3 and Ni-9Cr-6Al-0.3Y (in wt.%), respectively. In this study, 330 μm thick psz ceramic coatings on 125 μm thick NiCrAlY bond coat were deposited for the plasma thermal sprayed specimens. For the plasma thermal sprayed TBCs, the bond coats were deposited in vacuum to enhance the bonding strength and the ceramic coatings were deposited in air to provide some amount (3-5 vo.%) of porosities in the coatings. For the EB-PVD specimens, 120 μm thick psz ceramic coatings were deposited on the NiCrAlY bond coats with thickness of 75 μm . For these TBC specimens, the bond coats were aluminized to improve oxidation resistance prior to the psz ceramic coating application.

To characterize the oxidation products formed at the psz ceramic/bond coat interface during lifetimes of TBCs, the as-deposited specimens were exposed to the cyclic oxidation conditions. The cyclic oxidation tests were carried out every 65 minutes from 200°C to 1135°C in a furnace in air at atmospheric pressure. The 65 minute thermal cyclic oxidation test consisted of a 10 minute heat-up from 200°C to 1135°C, a 45 minute hold at 1135°C, followed by cooling to 200°C in 10 minutes. This procedure was repeated from 120 to 350 cycles, until the specimens showed at least 10% ceramic coating spallation. To investigate the reaction product development at the psz ceramic/bond coat interface, the cross-sections of the specimens, the spalled ceramic coatings as well as the spalled region on the metal were characterized. The heat-treated specimens were impregnated with epoxy resin in a vacuum jar and then dried in air to avoid fracture during sample preparation. The cross-sectional specimens were ground and polished to 0.25 μm using diamond paste. The experimental characterization was made using optical microscopy, SEM with EDS and X-



Fig. 2. Cross-sectional SEM photomicrograph of the as-deposited (plasma sprayed) TBC with psz coating of ZrO_2 -8wt.% Y_2O_3 .

ray diffractometer.

III. Results and Discussion

1. Plasma Thermal Sprayed TBCs

Fig. 1 and 2 show the SEM photomicrograph for the top surface and the cross-section of the as-deposited TBC. As seen in Fig. 1, the as-deposited psz ceramic coating is observed to consist of layered structure with cracks on the top surface. In Fig. 2, the upper region is the psz ceramic coating and the lower region is the bond coat. As seen in Fig. 2, the as-deposited ceramic coating is porous and no bond coat oxidation products are observed at the psz ceramic/bond coat interface for the as-deposited specimen.

After thermal cyclic oxidation for 230 cycles, the top surface of the psz ceramic coating was significantly degraded, showing the granular structure as seen in Fig. 3. A large quantity of bond coat oxidation product (primarily Al_2O_3) is observed at the psz ceramic/bond coat interface as

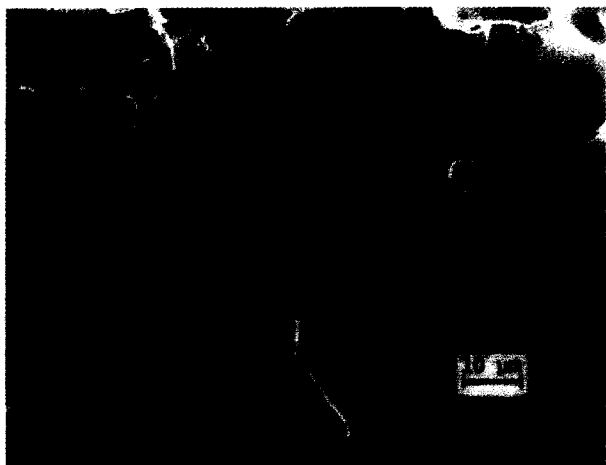


Fig. 1. SEM photomicrograph of the top surface of the as-deposited (plasma sprayed) psz coating of ZrO_2 -8wt.% Y_2O_3 .



Fig. 3. SEM photomicrograph of the top surface of the thermally cycled psz coating of ZrO_2 -8wt.% Y_2O_3 (plasma sprayed).

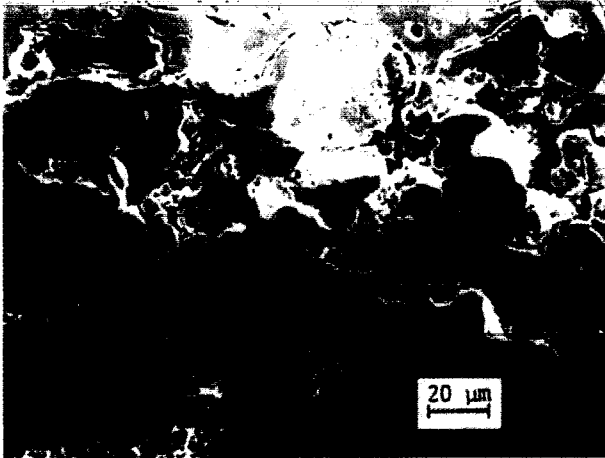


Fig. 4. Cross-sectional SEM photomicrograph of the thermally cycled TBC with psz coating of ZrO_2 -8wt.% Y_2O_3 .

seen in Fig. 4. A significant quantity of cracks developed within the psz ceramic coating after the thermal cyclic oxidation. The porosities and cracks in the thermally cycled psz coating provide the transport of oxygen, resulting in the oxidation of the underlying metallic bond coat. In addition, cracking is observed to have developed at the interface between the ceramic coating and the oxidation product and within the oxidation products as seen in Fig. 4. Fig. 5 presents the cross-sectional backscattered electron image (BEI) of the oxidation products formed at the psz ceramic/bond coat interface. In Fig. 5, the light grey region at the bottom portion is the bond coat and the dark grey region is the bond coat oxidation products. According to the EDXS analysis, the light grey region within the oxidation products contains Al, Cr, Ni and oxygen while the dark grey region contains primarily Al and oxygen. The EDXS data suggest that the grey region in the oxidation products would be a spinel such as $NiCr_2O_4$ or $Ni(Al,Cr)_2O_4$ and the dark region is Al_2O_3 . The white particles within the oxidation products are either



Fig. 5. Cross-sectional back scattered electron image of the oxidation products.

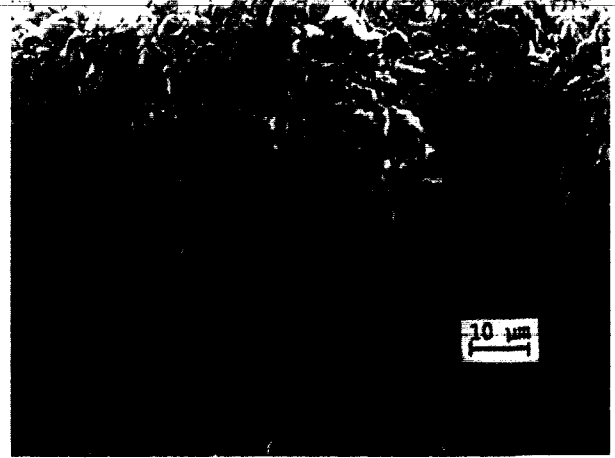


Fig. 6. SEM photomicrograph of the top surface of the as-deposited (EB-PVD) psz coating of ZrO_2 -8wt.% Y_2O_3 .

W/Mo/Cr rich phase or the metal particles which were imbedded during sample preparation. In Fig. 5, the fracture in the oxidation products is observed to have occurred in the light grey region. This experimental observation indicates that the fracture within the oxidation products takes place more easily in the region of the Cr/Ni rich oxides such as $NiCr_2O_4$ and $Ni(Al,Cr)_2O_4$ than Al_2O_3 . Thus, the formation of the Cr/Ni rich oxides would cause to the failure of TBCs during thermal cyclic oxidation.

2. Electron Beam-Physical Vapor Deposition TBCs

The SEM photomicrographs of the top surface and the cross-section for the as-deposited EB-PVD TBC specimen are presented in Fig. 6 and 7. As seen in Fig. 6 and 7, the as-deposited ceramic coating exhibits a columnar structure with a thin dense equiaxed layer near the psz ceramic/bond coat interface. This columnar structure has been reported to be strain-tolerant during thermal cyclic oxidation.^{10,11)} It is seen that the interface between the psz ceramic coating and the bond coat is smooth compared to

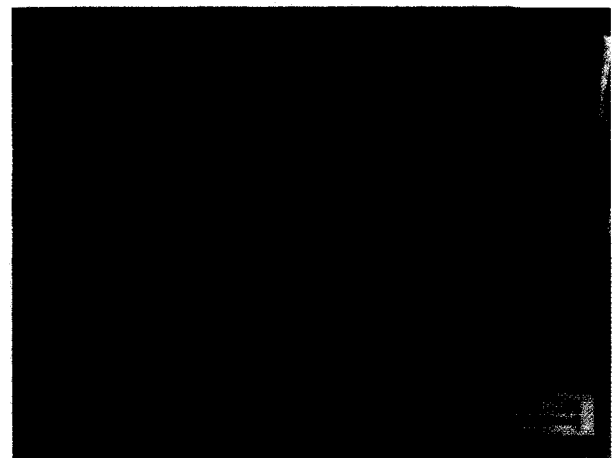


Fig. 7. Cross-sectional SEM photomicrograph of the as-deposited EB-PVD TBC.

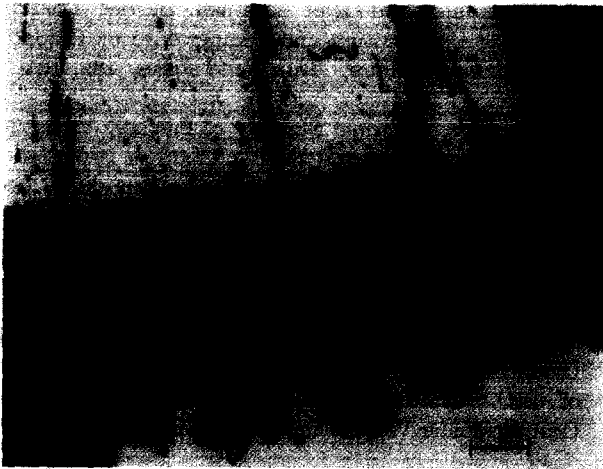


Fig. 8. Cross-sectional BEI of the thermally cycled EB-PVD TBC, showing the fracture within the oxidation products.



Fig. 9. Cross-sectional BEI of the oxidation products in the thermally cycled EB-PVD TBC.

the plasma sprayed TBCs. The roughness of the interface may influence the adhesion of the ceramic coating based on a mechanical keying mechanism of bonding.

The cross-sectional BEI photomicrographs of the oxidation products for the thermally cycled EB-PVD TBC specimen are presented in Fig. 8 and 9. In Fig. 8, the upper region is the psz ceramic coating and the lower region is the bond coat. The dark region in the center of the figure is the oxidation products. In Fig. 8, the grey region within the oxidation products is observed to consist of Al, Cr, Ni and oxygen and the dark region is Al_2O_3 . The Cr/Ni rich oxide developed near the psz ceramic coating would be formed by the outward diffusion of metal ion. The Al depletion in the bond coat due to the selective oxidation as well as the interdiffusion between bond coat and substrate lead to the coincident enrichment of other metals such as Cr and Ni in the bond coat. As a consequence, the selective oxidation of Al would not take place and the oxidation of other metal components (Cr, Ni) would begin. A continuous and dense Al_2O_3 layer

formed by the selective oxidation would depress the transport of oxygen through the Al_2O_3 layer, resulting in the outward diffusion of metal ions (such as Cr^{+3} , Ni^{+2}) through Al_2O_3 . These metal ions would form the oxides within the pre-existing Al_2O_3 near the ceramic coating. The white particles are mostly metal particles as seen in the plasma thermal sprayed TBCs. It is observed that cracking took place primarily at the interface between the dark region (Al_2O_3) and the grey region (Cr/Ni rich oxide) within the oxidation products as seen in Fig. 8. In Fig. 9, voids are found to have developed at the interface between the grey region (Cr/Ni rich oxide) and the dark region (Al_2O_3). This observation indicates that the formation of the voids at the interface between two different oxides should lead to the cracking within the oxidation products during cyclic oxidation.

IV. Conclusions

It was observed that the fracture in the TBCs took place within the NiCrAlY bond coat oxidation products, within the psz ceramic coating or at the interfaces in the TBCs during cyclic oxidation. It was also found that the fracture within these oxidation products occurred with the Cr/Ni rich oxides. Therefore, the formation of these oxides was a "life-limiting event" for TBCs.

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