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Bond Coat Oxidation and Hot Corrosion Behavior of Plasma Sprayed YSZ Coating on Ni Superalloy †

SAREMI Mohsen *, AFRASIABI Abbas ** and KOBAYASHI Akira ***

Abstract

Oxidation and hot corrosion are considered as two main destructive factors in thermal barrier coatings (TBCs). The mechanisms of bond coat oxidation and hot corrosion of yttria stabilized zirconia (YSZ) plasma sprayed coatings were evaluated. Oxidation tests were carried out at 1100 °C for 22,42 and 100 h. Hot corrosion tests were performed on the coating in molten salt ($\text{Na}_2\text{SO}_4+\text{V}_2\text{O}_5$) at 1050 °C for 40 h. Spallation was observed at the bond coat/YSZ interface after 100 h oxidation. Micro XRD analysis after the oxidation test revealed the formation of destructive oxides such as NiCr_2O_4 , NiCrO_3 and NiCrO_4 within the bond coat of YSZ coating. XRD and SEM studies after hot corrosion demonstrated the formation of monoclinic ZrO_2 and YVO_4 crystals as hot corrosion products, which caused the degradation of YSZ coating.

KEY WORDS: (Oxidation) (Hot corrosion) (YSZ) (Plasma spray)

1. Introduction

Thermal barrier coatings (TBCs) are widely used in gas turbines to reduce thermal effects and increase turbine efficiency. The TBCs are usually composed of a MCrAlY bond coat (M=Ni or Co) as an oxidation resistant layer and yttria stabilized zirconia (YSZ) as a top coat that provides thermal insulation for the metallic substrate¹⁻⁶⁾. However there are shortcomings such as spallation, hot corrosion and phase transformation, which reduce the durability of the coating⁷⁻⁹⁾.

Application of TBC at high temperature causes the transfer of oxygen through the top coat towards the bond coat, so an oxidized scale can be formed on the bond coat which is termed the thermally grown oxide (TGO). Although this scale protects the substrate against further oxidation, the growth of TGO during thermal cycling leads to the failure of the YSZ layer¹⁰⁻¹⁵⁾.

Two mechanisms have been proposed for oxygen transfer through plasma sprayed zirconia coatings: ionic diffusion from the crystalline structure of ZrO_2 and gas penetration through porosities and micro cracks¹⁶⁻¹⁷⁾.

The thickness of oxide scale (TGO) increases during an oxidation process and is accompanied by stress at the interface of bond coat and YSZ layer. Sometimes, this stress is more than the strain tolerance of TBC, thus the delamination of coating can occur at the YSZ/bond coat

interface¹⁸⁻²¹⁾.

Hot corrosion is due to the use of low quality fuels which usually contain impurities such as Na and V, which then can form Na_2SO_4 and V_2O_5 salts on the surface of turbine blades. Such fused salts can react with yttria (the stabilizer component of YSZ) and cause transformation of tetragonal or cubic zirconia to the monoclinic phase during cooling. This transformation is accompanied by 3-5% volume expansion, leading to cracking and spallation of TBCs. In spite of many efforts in this regard, the failure mechanism of TBCs during oxidation and hot corrosion has not clearly been explained.

In this study, a NiCrAlY bond coat and a YSZ top coat were applied on In-738 super alloy using a plasma spray method and the failure behavior of the coating during oxidation and hot corrosion has been investigated.

2. Experimental Procedure

2.1. Materials and coating preparation

Nickel based superalloy (Inconel 738) disks of ($\phi 25 \times 10\text{mm}$) which had been grit blasted with alumina particles were used as substrates. Two types of commercial powders were selected: Amdry 962 (Ni-22Cr-10Al-1Y , $-106+52\mu\text{m}$) as bond coat, Metco 204 NS-G ($\text{ZrO}_2\text{-8\%Y}_2\text{O}_3$, $-106+11\mu\text{m}$) as top coat.

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The layers of coating were prepared by the plasma spray method. The thicknesses of bond coat and top coat were 150 and 350 μm respectively. **Table 1** indicates the parameters of plasma spraying

2.2. Oxidation and hot corrosion tests

For oxidation tests, the as-sprayed coatings were put in an electric furnace with an air atmosphere at 1100 °C for 22, 24 and 100 hours. For hot corrosion tests, a mixture of 55 wt.% V_2O_5 and 45 wt.% Na_2SO_4 powders was selected as corrosive salt. Some physical specifications of each salt are presented in **Table 2**. The corrosive salt was spread over the surface of the coating in a concentration of 30 mg/cm^2 leaving 3mm distance from the uncoated edge to avoid edge effects. The specimens were put in an electric furnace with air atmosphere at 1050°C for 40 hours and then cooled down inside the furnace and were inspected periodically every 8 hours.

2.3. Microstructure and chemical analysis

All of the samples were sectioned with a diamond saw, cold epoxy mounted and fine polished. The microstructure and chemical composition of coating were examined by scanning electron microscopy (SEM, Cambridge, Cam scan – MV 2300, U.K.) equipped with energy dispersive spectrometer (EDS). X – ray diffraction (XRD) was performed on the surface of YSZ coating before and after hot corrosion. Micro – XRD (JEOL, JDX – 3530 M, Japan) with acollimator of 50 μm was carried out on the cross section of the bond coat after oxidation to determine the crystalline structure of oxide scales.

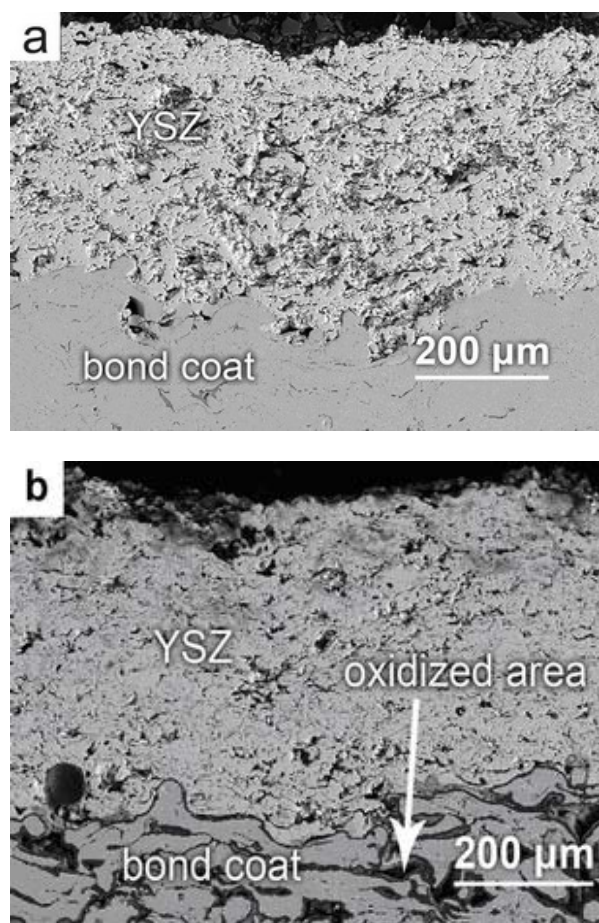


Fig. 1 SEM images showing the cross section of coating: (a) as sprayed; (b) after oxidation at 1100 °C for 100 h.

Table 1 Parameters of plasma spraying.

Parameter	NiCrAlY	YSZ
Current (A)	400	550
Voltage (V)	75	70
Primary gas, Ar (l/min)	57	38
Secondary gas, H ₂ (l/min)	17	17
Powder feed rate (g/min)	45	35
Spray distance (cm)	15	7.5

Table 2 Physical specifications of salts.

Type of salt	Melting point °C	Density(g/cm ³)
Na_2SO_4	884	2.7
V_2O_5	690	3.3

3. Results and discussion

3.1. Microstructure and crystalline structure after oxidation

Figure 1a shows the cross section of the YSZ layer and bond coat. The coating showed the lamellar structure which is the characteristic of plasma sprayed coatings. **Figure 1b** shows the cross section of YSZ coating after 100 h oxidation at 1100 °C. An oxide scale (TGO) was formed on the bond coat, due to oxygen penetration through the ceramic layer. TGO scale has been exhibited with high magnification in Fig. 4. In addition, oxygen penetrated through open porosities of NiCrAlY layer, so oxide scales were formed within bond.

Figures 2 and 3 exhibit the cross sectional line scan before and after oxidation at 1100 °C for 100 h. The comparison of the line-scanned images demonstrates the concentration and distribution of Ni and Cr have no substantial changes before and after oxidation, while the concentration of O and Al increased at the interface of bond coat/YSZ after oxidation, which indicates the presence of Al_2O_3 at the mentioned interface. In addition, the amount of Al decreased in internal zones of the bond coat.

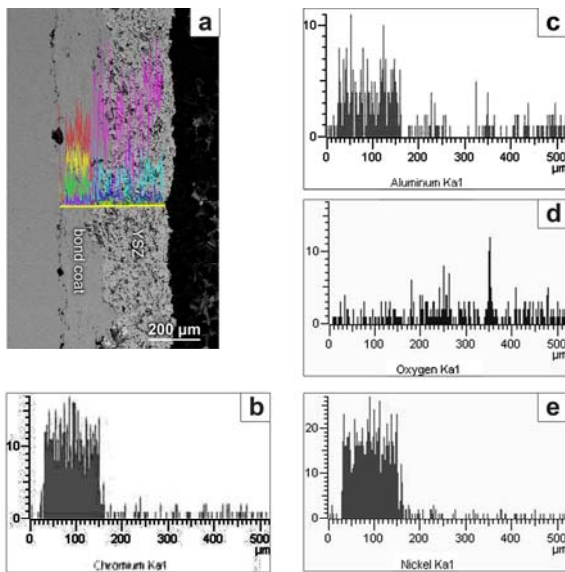


Fig. 2 Cross sectional line scan images from as-sprayed coating: (a) SEM image; (b) Cr; (c) Al; (d) O; (e) Ni line scans of (a).

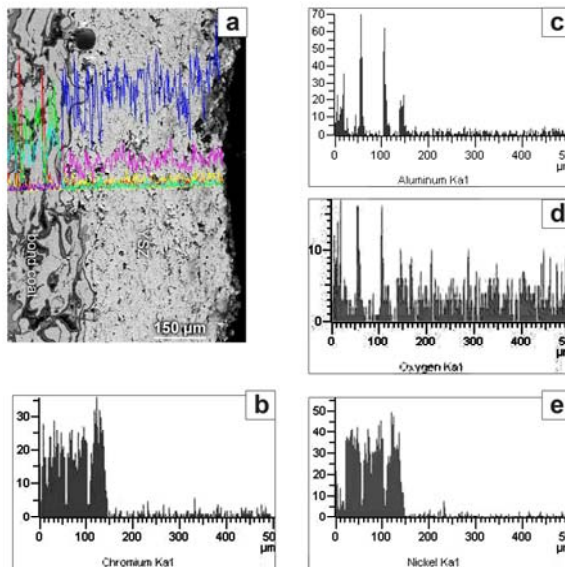


Fig. 3 Cross sectional line scan images from coating after oxidation at 1100 °C for 100 h: (a) SEM image; (b) Cr; (c) Al; (d) O; (e) Ni line scans of (a).

Figure 4 shows the thermally grown oxide (TGO) after oxidation at 1100 °C. According to thermodynamic considerations, Al has high affinity for reaction with O, so Al diffusion and O penetration lead to Al_2O_3 formation at the interface of bond coat/YSZ²²⁻²³.

The examination of TGO by EDS indicated the high percentage of Al and O (**Fig. 5**) and less amount of Ni

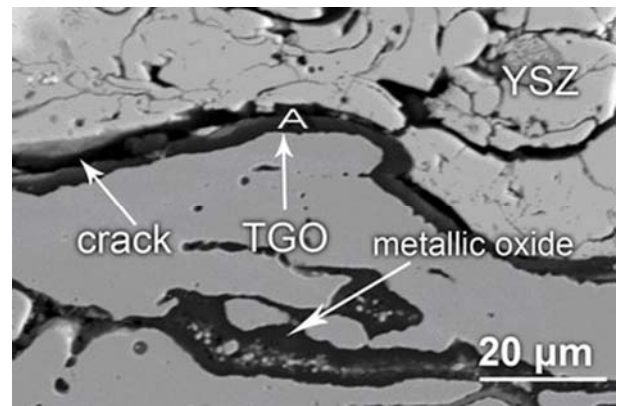


Fig. 4 Microstructure at the bond coat /YSZ interface after oxidation at 1100 °C for 100 h, showing spallation at TGO/YSZ interface.

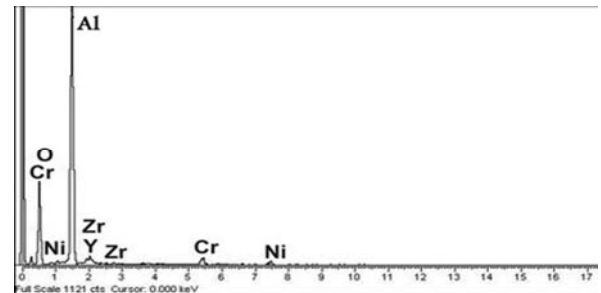


Fig. 5 EDS analysis from TGO at point A in Fig. 4.

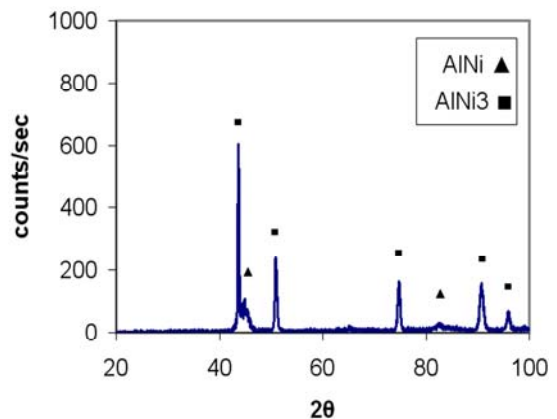


Fig. 6 XRD pattern from the surface of the as-sprayed bond coat.

and Cr elements, Thus the TGO comprises mainly Al_2O_3 . As shown in Fig. 4, crack and spallation occurred at the TGO/YSZ interface due to grown oxide. As mentioned above, oxygen penetrated through interconnected porosities and the internal areas within the bond coat were oxidized. The EDS analysis from different

points of these oxides showed the presence of Ni, Cr, Al and O elements. X-ray diffraction (XRD) analysis from the surface of the as-sprayed bond coat has been presented in **Fig. 6** which shows the NiAl (β) and Ni₃Al (γ') phases. **Figure 7** exhibits the cross sectional micro-XRD analysis from the bond coat after oxidation

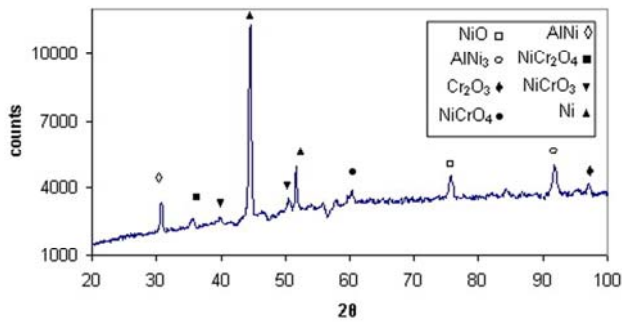


Fig. 7 Micro XRD patterns from the cross section of bond coat after oxidation at 1100 °C for 100 h.

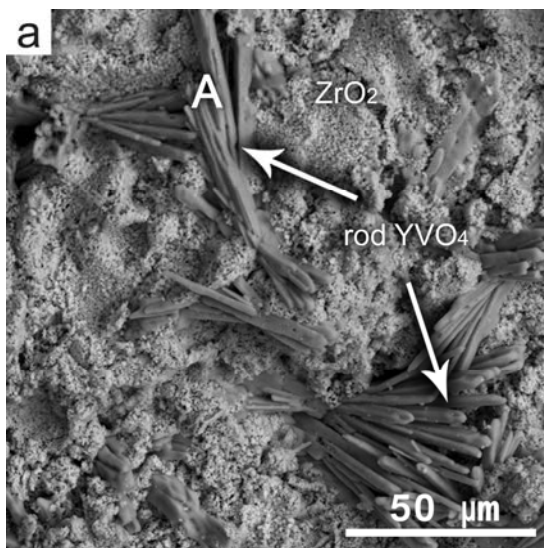


Fig. 8 SEM micrograph from YVO₄ crystals on the surface of coating after hot corrosion.

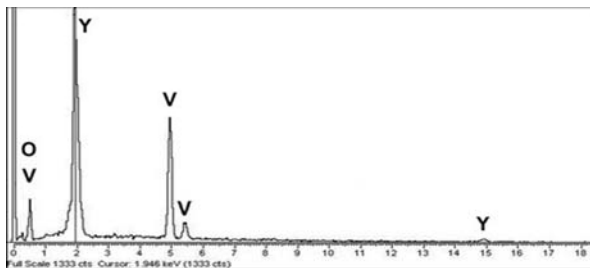


Fig. 9 EDS spectrum from rod crystals at point A in Fig. 8.

at 1100 °C for 100 h. The oxide phases in bond coat are: NiCr₂O₄, NiCrO₃, NiCrO₄, Cr₂O₃, and NiO.

According to previous investigations, the formation of NiCr₂O₄, NiCrO₃, NiCrO₄ oxides is accompanied with rapid volume increase²⁴ which generates localized stress and leads to spallation of the ceramic layer from the bond coat (Fig. 4).

3.2. Surface morphology and crystalline structure after hot corrosion

Figure 8 shows the SEM surface morphology from the coating after 40 h of hot corrosion testing. YSZ coating after hot corrosion revealed a porous surface and many rod crystals, which deposited on the surface. EDS analysis from the surface (**Fig. 9**) demonstrated that the crystals were composed of yttrium, vanadium and oxygen, and they were identified by XRD analysis to be YVO₄.

XRD analysis was performed on the surface of the coating before and after hot corrosion testing. **Figure 10** illustrates the XRD patterns of as sprayed YSZ. **Figure 11** shows the XRD patterns from the coating after hot corrosion testing.

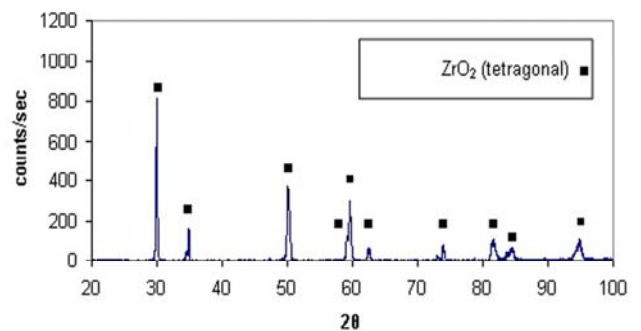


Fig. 10 XRD patterns from the surface of the as sprayed YSZ.

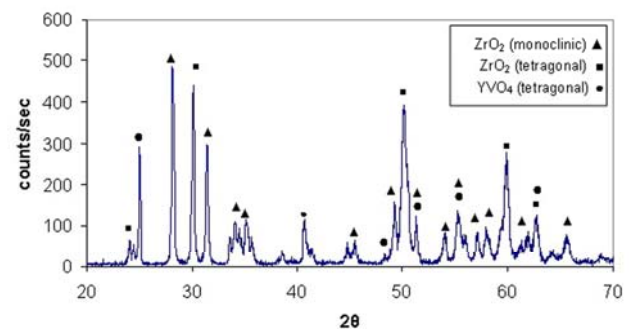


Fig. 11 XRD patterns from the surface of the YSZ coating after hot corrosion.

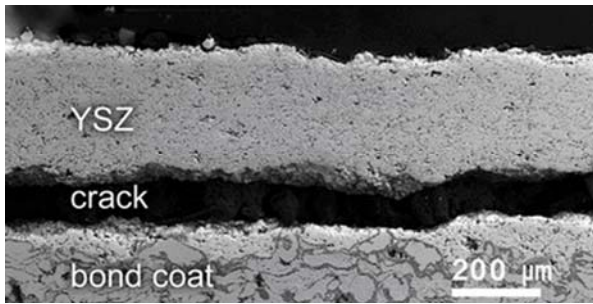
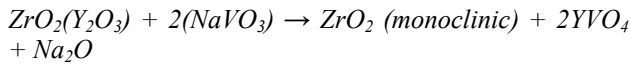
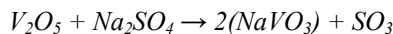


Fig. 12 SEM image showing the cross section of the coating after hot corrosion test.

Monoclinic ZrO_2 and YVO_4 were formed in the coating after exposure to molten salt at 1050 °C for 40 h. The cross section of the coating after hot corrosion testing is exhibited in **Fig. 12**. The wide crack in YSZ coating (Fig.12) is the result of formation of the monoclinic ZrO_2 and YVO_4 crystals.

The mechanism of degradation during hot corrosion can be explained by the following reactions ²⁵⁾:



At first $NaVO_3$ was formed after the reaction of fused salts (55 wt. % V_2O_5 + 45 wt. % Na_2SO_4), then $NaVO_3$ reacted with Y_2O_3 , resulting in the formation of monoclinic ZrO_2 , YVO_4 and Na_2O . It should be noted that the EDS analysis was performed on different points of the surface and cross section of the coatings, but Na was not detected. It appears that Na_2O is sublimated at the temperature of hot corrosion testing.

The hot corrosion behavior and failure mechanism of TBCs in the present study comprises the following steps:

- a) Molten salt penetration through microcracks and open porosities.
- b) Reaction of molten salt with the stabilizer of zirconia (Y_2O_3).
- c) Phase transformation of zirconia from tetragonal to monoclinic, due to the depletion of stabilizer, which is accompanied by volume expansion of the coating.
- d) Formation of YVO_4 crystals with rod shape that grow out from the of surface and cause additional stresses in the coating.
- e) Formation of horizontal cracks in the ceramic layer due to the production monoclinic zirconia and YVO_4 crystals.

4. Conclusion

- (1) During oxygen penetration through the YSZ coating, a TGO layer was formed along the interface between the bond coat and the YSZ layer, which consists mainly of Al_2O_3 . The growth of the TGO layer and destructive oxides such as $NiCr_2O_4$, $NiCrO_3$ and $NiCrO_4$ inside the bond coat produced tensile stress at the interface of the bond coat/YSZ after oxidation which led to delamination of the YSZ layer from bond coat.
- (2) During hot corrosion of the YSZ coating, molten salt penetration through microcracks and open porosities caused the reaction of corrosive materials with the stabilizer of zirconia (Y_2O_3) which led to formation of YVO_4 crystals and phase transformation of zirconia from tetragonal to monoclinic. Horizontal cracks and spallation of YSZ layer are due to formation of the monoclinic zirconia and YVO_4 crystals.

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