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Evaluation of TBC-Coated β-NiAl Substrates Without a Bond Coat

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Abstract

β-NiAl substrates with various alloy additions and oxide dispersions were coated with Y_2O_3-stabilized ZrO_2 using electron beam-physical vapor deposition. Cyclic oxidation experiments (1000°-1200°C) were conducted to study the effect of substrate dopants such as Y and Zr on coating lifetime without the intermediate metallic bond coat layer used in conventional thermal barrier coatings. Oxidation kinetics and Al_2O_3 scale microstructures were compared to those for uncoated substrates. Degradation of the substrate-alumina interface by void formation was the primary mechanism leading to coating spallation. Coating lifetime was correlated to alumina scale adhesion on the uncoated substrates.

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Introduction

Currently, commercial thermal barrier coating (TBC) systems consist of a substrate, a metallic bond coat and a ceramic coating applied either by plasma spraying (PS) or electron beam-physical vapor deposition (EB-PVD)[1-6]. The ceramic coating is commonly yttria-stabilized zirconia (YSZ) because of its low thermal conductivity and high coefficient of thermal expansion. The bond coat is typically chosen to be resistant to both thermo-mechanical fatigue and oxidation, as the YSZ coating is essentially transparent to oxygen and thus does not protect the substrate.

The current work has focused on β-NiAl substrates which are sufficiently oxidation resistant that they do not require a bond coat. From an engineering viewpoint, eliminating the bond coat from the TBC is a potential cost saving that would also reduce the weight and thickness of the coating and make it easier to repair. From a scientific viewpoint, it simplifies the system which makes it easier to characterize and allows for a more fundamental study of the oxidation process and coating failure. This project has focused on EB-PVD YSZ coatings because they do not require a rough substrate surface (such as that required by a PS coating).

Though not of sole importance[3-6], oxidation of the bond coat is a primary failure mechanism of commercial TBC's. In most cases, bond coats are designed to form an external, protective α-Al_2O_3 scale during high temperature oxidation, similar to that found on β-NiAl. Relevant issues include the effect of the YSZ top coat on the oxidation rate and oxidation product and the effect of reactive element (RE) additions (such as Y and Zr), particularly on oxide adherence.

Experimental Procedure

This paper is a compilation of experiments conducted at General Electric Aircraft Engines and Oak Ridge National Laboratory and thus includes a range of alloys and experimental conditions. The chemical compositions of the substrates investigated in these experiments are shown in Table I. Bulk sulfur contents were determined by LECO testing. Test samples were generally disks of 10-20 mm diameter and 1-2 mm thick. All of the samples were coated on one face (and partially around the circumference) with an approximately 125 µm (5 mil) thick coating of 7-8wt%Y_2O_3-ZrO_2 deposited by EB-PVD (half-coated).

Both isothermal and cyclic oxidation tests were performed. In all of the oxidation tests there was no thermal gradient across the coating. Cycle times are listed as time at temperature, followed by cooling to room

Table I. Chemical composition of the substrate alloys in atomic percent. The first 3 are nominal compositions while the others were determined by inductively coupled plasma analysis.

Alloys	Undoped NiAl	NiAl + Y	Rene 142	NiAl + Zr	NiAl + Al_2O_3	NiAl + Y_2O_3	NiAl + ZrO_2
Crystallinity:	single	single	poly	poly	poly	poly	poly
Ni	50	49.9	bal.	50.04	49.89	47.81	49.08
Al	50	50	13.1	49.65	47.31	47.62	48.29
Fe				0.02	0.15	0.02	0.03
Cr			7.6	<0.01	0.05	0.04	0.03
Si				0.21	0.21	0.10	0.18
Other			11.8 Co 2.1 Ta 0.9 Mo	<0.01 Y	<0.01 Zr	<0.01 Zr	<0.01 Y
Dopant	--	0.1 (Y)	0.81 Hf	0.04 Zr	0.005 Y	0.19 Y	0.28 Zr
C				0.02	< 0.01	< 0.01	0.11
O				0.02	2.11	3.77	1.76
S (in ppm)	n.d.	n.d.	n.d.	35	< 3	< 3	4

temperature. The isothermal kinetics were measured using a Cahn Instruments, Model 1000 microbalance. After oxidation, the coatings were characterized using a scanning electron microscope (SEM) equipped with an energy dispersive x-ray detector (EDX).

Results

Coated specimens of single crystal β-NiAl alloys, with and without Y (Table I), were thermally cycled in air for 0.75h cycles in a bottom drop furnace. The first 1020 cycles were at 1093°C (2000°F), after which the temperature was increased to 1135°C (2075°C) and the test continued until the coatings spalled. Representative data from selected samples is given in Table II.

Upon failure, the coatings were sectioned and examined using SEM/EDX. Failure generally occurred at the metal-Al_2O_3 scale interface with only a few exceptions. An average scale thickness was measured for each sample, Table II. Due to the change in test temperature, it was not possible to accurately determine an oxidation rate based on scale thickness. However, an estimation was made which proved to be the same order of magnitude as values given in the literature[7]. In general, the Y addition did not improve coating lifetime but did appear to reduce the oxidation rate, Table II.

Table II. Results from coated (on one side) NiAl substrates during 0.75 h cycles at 1093°-1135°C.

Substrate	Cycles to Failure	Oxide Thickness (µm)	Estimated Parabolic Rate (g^2/cm^4s)
NiAl	2640	8.5	3.4 x 10^{-13}
NiAl	2640	8.5	3.4
NiAl	2320	9.5	4.9
NiAl	2040	9.3	5.3
NiAl + Y	2040	4.9	1.5

Examination (by EDX) of the YSZ/alumina interface showed the presence of Ni-rich oxide, presumably the $NiAl_2O_4$ spinel phase, Figure 1. This is somewhat surprising as β-NiAl is an excellent alumina-former and generally does not form Ni-rich oxides during transient or steady-state oxidation[8-9]. No Ni-rich oxide was observed on specimens examined after shorter oxidation times. Formation of a Ni-rich oxide layer above an otherwise adherent alumina scale has been observed during Ni_3Al cyclic oxidation and attributed to cracking of the alumina scale[10]. On conventional TBC-coated substrates (metallic bond coat on superalloy substrate), spinel layers are routinely observed at the YSZ/Al_2O_3 interface and coarsen with continuing cyclic exposure[11,12].

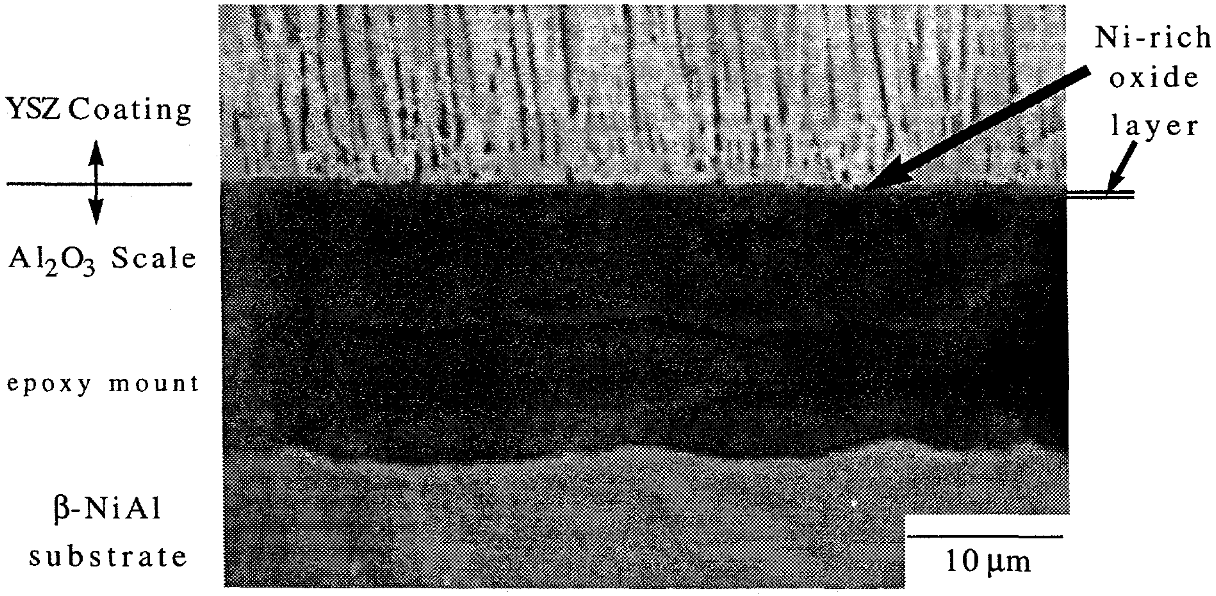

Figure 1. SEM backscattered electron image of an epoxy-mounted, polished cross-section showing the spalled YSZ coating and thermally grown Al_2O_3 scale adjacent to the undoped NiAl substrate after oxidation for 2040 0.75 h cycles. A Ni-rich layer (presumably $NiAl_2O_4$) is observed at the YSZ/Al_2O_3 interface. Failure occurred at the metal-scale interface.

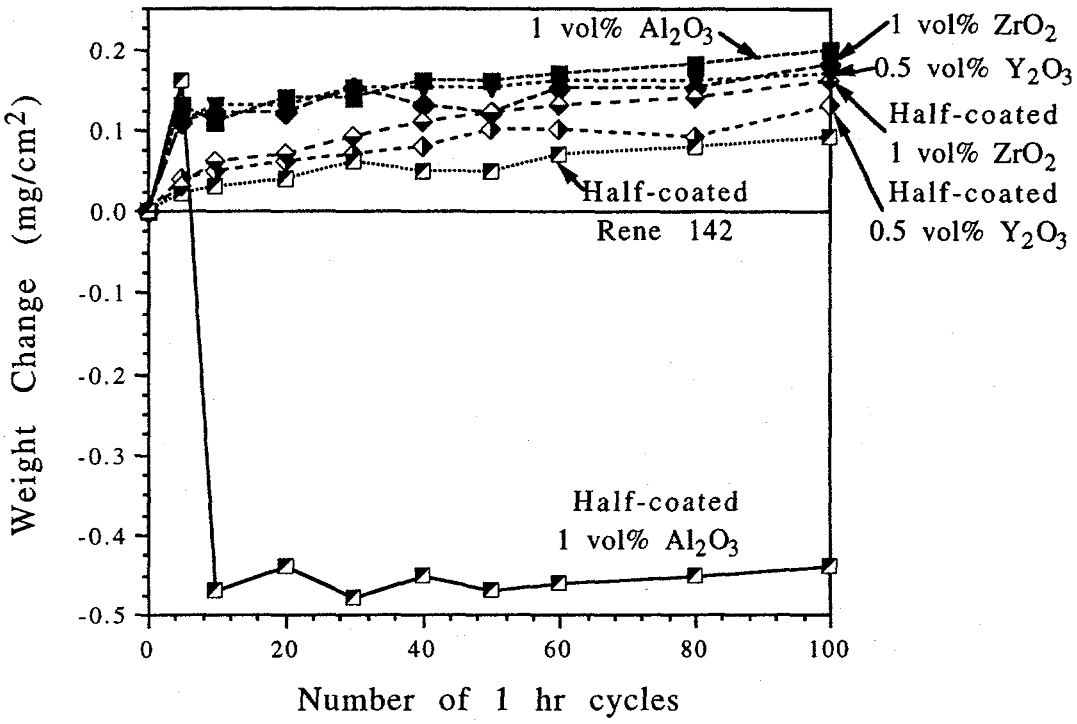

Figure 2. Weight change of various uncoated and half-coated (125 µm thick YSZ on one side) oxide-dispersed β-NiAl alloys cycled from room temperature to 1000°C.

In another set of experiments, coated and uncoated coupons of NiAl containing dispersions of Y_2O_3, ZrO_2 and Al_2O_3 (processing details are included elsewhere[13,14]) were exposed for 1 h cycles in air at 1000°C (1832°F) in alumina crucibles. To date, 100 cycles have been completed, Figure 2. A conventionally coated Rene 142 coupon was also included in this test for comparison. Due to the low temperature, very little weight gain was measured and almost no spallation was observed. A small amount of coating spalled from the side of the Al_2O_3-dispersed NiAl resulting in a weight loss, but otherwise no significant differences were noted between the coated and uncoated samples or the various dispersions. Weight gains in these tests were similar to those measured isothermally[15].

In order to induce coating failure, coated samples of oxide-dispersed β-NiAl also were cycled at 1200°C (2192°F). In this case, the cycle time was 2 h and the samples were hung by Pt-Rh wire in a vertical furnace in 1 atm dry, flowing O_2. These samples exhibited a much faster oxidation rate (approximately 1.5 µm Al_2O_3 formed during the first 2 h exposure[16]), and failed more quickly. These data also allowed some differentiation of the effects of the different oxide dispersions, Figure 3. The Al_2O_3-dispersed β-NiAl began to spall after the first cycle and the coating had completely spalled after the 2nd cycle at 1200°C. The ZrO_2-dispersed substrate spalled completely after the 16th cycle, whereas the Y_2O_3-dispersed

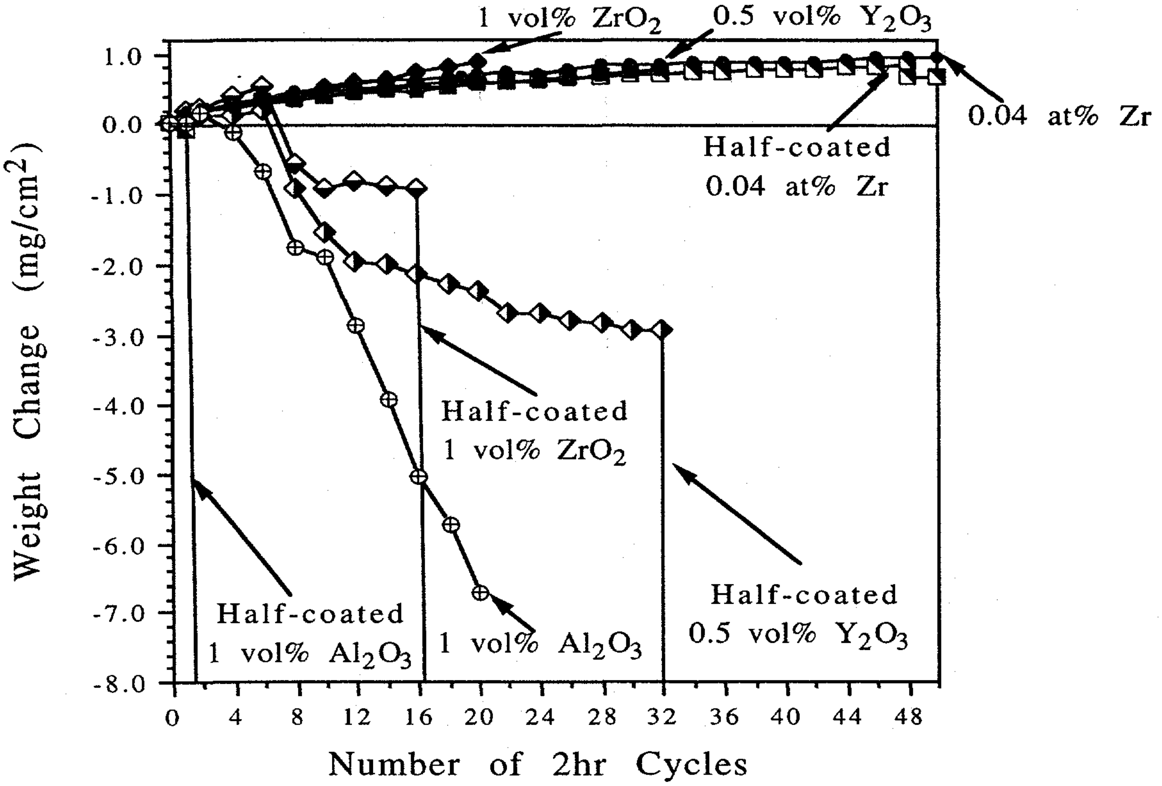

Figure 3. Weight change of various uncoated and half-coated (125 µm thick YSZ on one side) oxide-dispersed and Zr-doped β-NiAl alloys cycled from room temperature to 1200°C. The large weight losses occurred due to complete spallation of the YSZ coating.

sample did not spall completely until after 32 2h cycles. These samples showed some weight loss prior to complete coating failure because the coating chipped off the circumference. The longest coating life was observed for a poly-crystalline NiAl + 0.04at%Zr substrate. To date, this sample has been cycled 50 times with only slight chipping at the edge.

In general, these coating lifetimes can be correlated with oxide adherence on uncoated substrates[13,14,16]. Uncoated, Al_2O_3-dispersed NiAl spalled readily after each cycle at 1200°C, while Zr-doped NiAl showed little evidence of spallation even after 50 cycles (Figure 3).

The Zr- and Y_2O_3-doped substrates also were isothermally exposed for 200h at 1200°C to measure the oxidation rate. Measured rates were 2-6 x 10^{-12} g^2/cm^4s, the same range as observed for uncoated alumina-formers containing Y or Zr additions[7,9,13,14,17]. On cooling, the coating completely spalled from the Y_2O_3-dispersed substrate at the metal-scale interface. SEM analysis of pieces of spalled coating, Figure 4, showed the typical columnar structure of an α-Al_2O_3 scale[14,17,18] attached to the YSZ coating. No evidence of Ni-rich spinel formation was observed. The coating on Zr-doped NiAl did not spall at all after the 200h exposure.

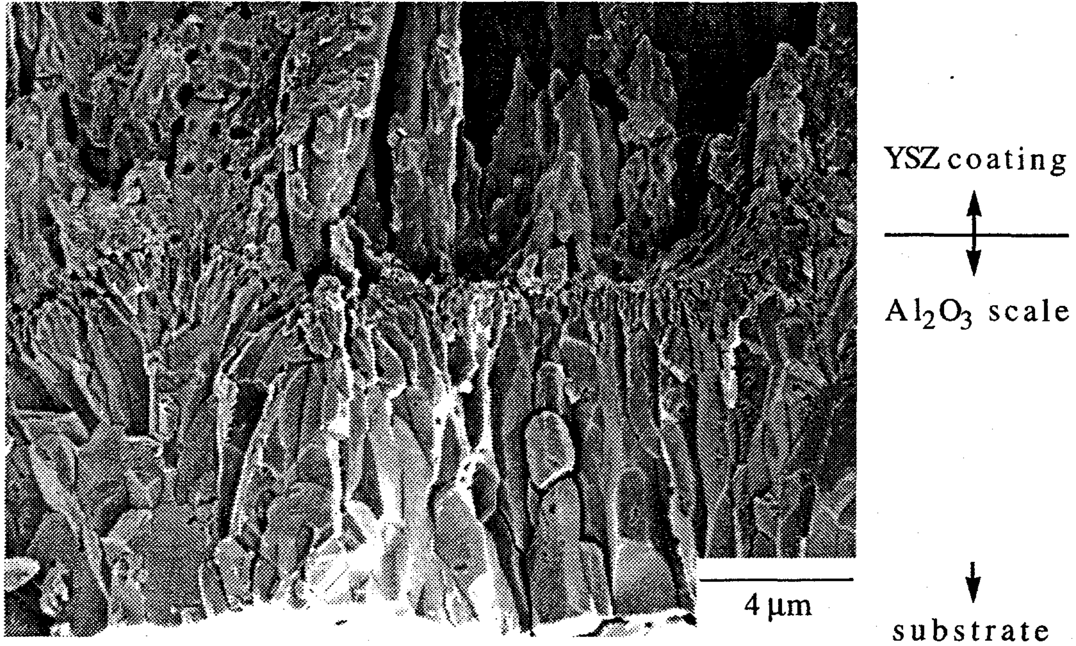

Figure 4. SEM secondary electron image of a cross-section of the spalled alumina scale/YSZ coating, formed after oxidation for 200h at 1200°C on Y_2O_3-dispersed β-NiAl. The columnar structure of the alumina scale is typical of reactive element-doped alumina scales formed at this temperature.

For the oxide-dispersed β-NiAl substrates, all of the failures from both cyclic and isothermal testing were observed to occur at the NiAl-Al_2O_3 interface. This type of failure is similar to that observed at lower temperatures (Figure 1) and reported in the literature[4,6]. For the failed samples at 1200°C, no evidence of Ni-rich oxide formation was found at the YSZ/Al_2O_3 interface. Characterization of the metal-scale interface showed in each case the presence of interfacial voids. An example is shown in Figure 5 where faceted alumina grains imprinted the metal surface in some areas, but in other areas voids at the NiAl/Al_2O_3 interface resulted in a smooth metal surface. It appears that above the voids, a ridge-type structure formed in the oxide[19]. Interfacial void formation during oxidation is widely observed and the presence of reactive elements (REs) such as Y and Zr have been shown to inhibit void formation[8,19-22]. Overall, adhesion of the thermally-grown alumina scale appeared to be a primary factor in all of the failures.

Discussion

β-NiAl substrates provide a model system for the study of oxidation-related TBC failure mechanisms for a number of reasons. By coating the highly oxidation-resistant NiAl substrate, it was possible to characterize the oxidation process beneath the YSZ coating without the formation of

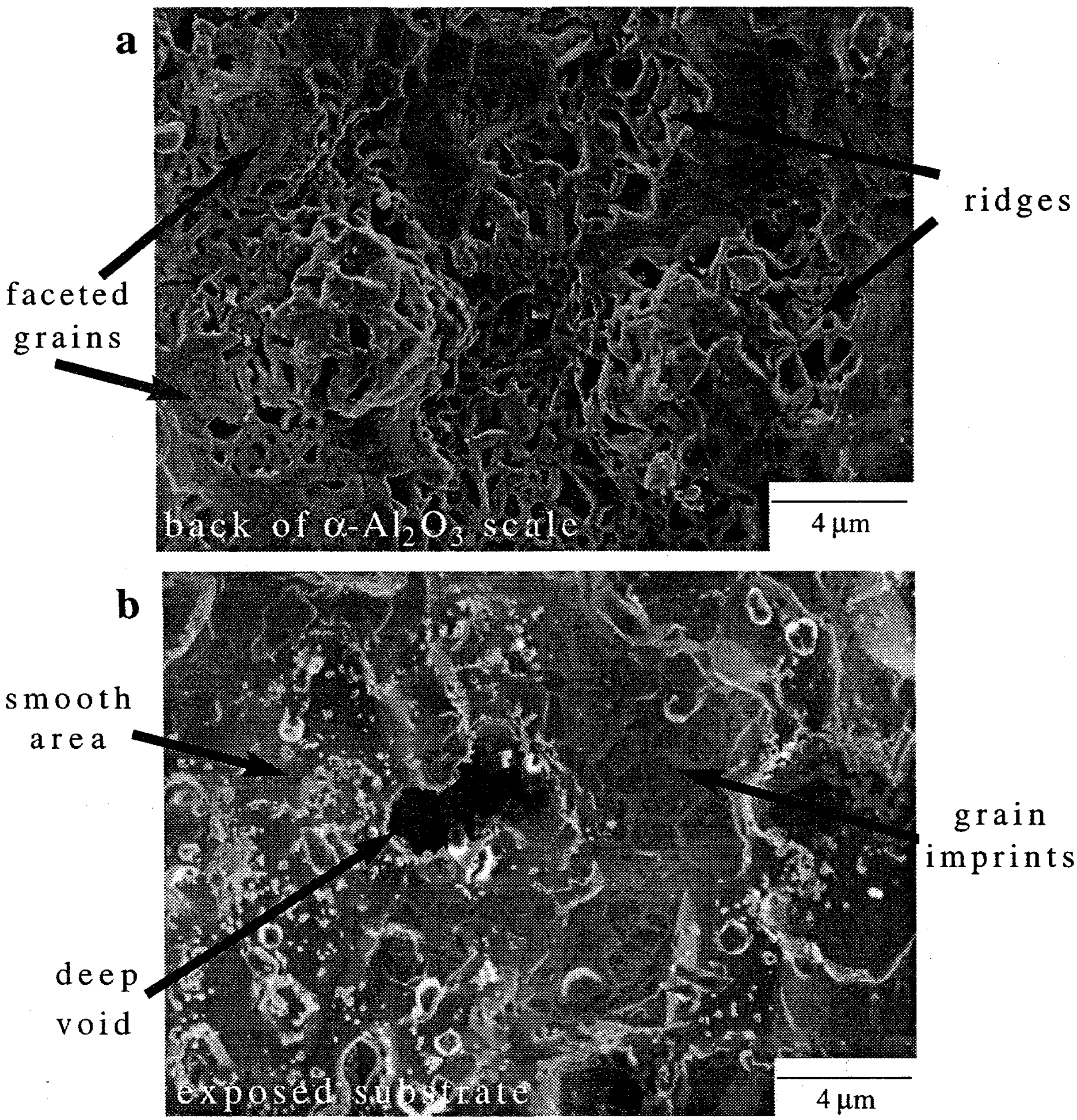

Figure 5. SEM secondary electron images of YSZ-coated ZrO_2-dispersed β-NiAl after oxidation for 16, 2-h cycles at 1200°C: (a) the spalled alumina scale surface in plan view adjacent to the substrate; and (b) the substrate exposed by the spallation in plan view[16]. The ridged areas appear to form when contact is lost with the substrate. Some interfacial voids, e.g. near the center of (b), become quite deep.

transient (base metal) oxides. Also, failure of the coatings did not involve Al depletion of the substrate (as observed in bond coats[4,11]) or any breakaway (rapid) oxidation of the substrate. Furthermore, because the substrates did not include the wide range of elements generally found in superalloys and their bond coats, there was no migration of extraneous elements into the oxide[12], which further complicates characterization.

Because the coating is essentially transparent to oxygen, it appears that there is little effect of the coating on the formation of Al_2O_3 on β-NiAl. The oxidation rate was not changed by the coating nor was the scale microstructure. On less oxidation-resistant substrates, it is possible that the YSZ coating could have more of an effect, particularly during the transient stage of oxidation, when base-metal, spinel-type oxides or metastable alumina phases can form. The formation of spinel at the YSZ/Al_2O_3 interface in some cases was unusual for the oxidation of β-NiAl. No Ni-rich oxide was detected in a TEM cross-section of a YSZ-coated Zr-doped NiAl sample oxidized for 2h at 1200°C[23]. However, long-term cycling at lower temperatures may result in spinel formation.

The adhesion of the alumina scale is extremely important in the case of a TBC, where scale spallation means the loss of the YSZ coating. For these samples, the primary cause of spallation appeared to be the nucleation and growth of interfacial voids, which is a widely observed but poorly understood phenomenon in high temperature oxidation[8,14,16,17,19-25]. Void growth reduces contact between the substrate and oxide and leads to failure at that interface, usually during cooling when the different expansion coefficients create shear stresses at the interface. It has been proposed[19,24,25] that interfacial segregation of indigenous sulfur changes the surface energies, which accelerates the growth of interfacial voids. By desulfurizing (below 1ppm)[26-28] or by RE-doping (which has been found to lower the S activity[28] and alleviate the detrimental effect of S[25-29]), this mechanism would be inhibited. In this study, the substrates were not de-sulfurized and no correlation could be made between S content and coating lifetime. The higher sulfur level in Zr-doped NiAl (Table I) was apparently offset by the Zr addition.

The effect of Y and Zr additions was more pronounced at 1200°C than at 1000°C-1135°C. Thinner scales are generally more adherent because they generate lower stresses on cooling. Adhesion of thicker alumina scales, either because they are grown at higher temperature or for longer times, is usually improved by RE additions[14,17,20,25,27,29]. Some reduction of the scale growth rate was observed with RE doping (Table II) and has been reported in the literature[9,14,17,25,29,30], but does not appear to be of primary importance in improving scale adhesion. Current mechanistic models generally recognize some interaction between indigenous S and RE-doping in determining scale adhesion but no single model is widely accepted.

Conclusions

(1) A YSZ coating does not modify the oxidation rate or significantly

change the α-Al_2O_3 microstructure grown on β-NiAl.

(2) As observed with other EB-PVD coatings, spallation occurred primarily at the metal substrate-Al_2O_3 interface.

(3) Coating lifetime in cyclic testing was primarily dependent on the Al_2O_3 scale adhesion. Substrates on which coatings had longer life demonstrated better oxide scale adhesion when tested without a coating.

(4) Failure at the metal-scale interface was accompanied by the formation of interfacial voids.

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