Evaluation of Thermal Barrier Coating Systems on Novel Substrates

B.A. Pint, I.G. Wright, and W.J. Brindley

Testing was conducted on both plasma-sprayed (PS) and electron beam-physical vapor deposited (EB-PVD) Y_2O_3-stabilized ZrO_2 (YSZ) thermal barrier coatings (TBCs) applied directly to oxidation-resistant substrates such as β-NiAl, oxide-dispersed FeCrAl, and NiCr. On an alloy that forms a very adherent alumina scale, β-NiAl + Zr, the coating lifetime of YSZ in furnace cyclic tests was 6 or more times longer than on state-of-the-art, YSZ coatings on single-crystal Ni-base superalloys with MCrAlY or Pt aluminide bond coats. Coatings on FeCrAl alloys appear to be a viable option for applications such as the external skin of the X-33, single stage to orbit, reusable launch vehicle. Model chromia-forming bond coat compositions also show promise for power generation applications at temperatures where hot corrosion may be a major problem. In general, while this work examined unique materials systems, many of the same fundamental failure mechanisms observed in conventional TBCs were observed.

Keywords	thermal barrier coatings, NiAl, FeCrAl, NiCr, chromia, alumina, X-33 reusable launch vehicle

1. Introduction

Thermal barrier coatings (TBCs) were developed to extend the useful lifetime of Ni-base superalloys in the hot section of turbine engines by lowering the metal temperature, thus reducing thermal fatigue and increasing lifetime of the component.[1–6] The ceramic top coat is typically Y_2O_3-stabilized ZrO_2 (YSZ), which has a low thermal conductivity, is inert in combustion environments, and has a coefficient of thermal expansion reasonably compatible with Ni-base superalloys. However, because YSZ is essentially transparent to the transport of oxygen, oxidation of the metallic substrate occurs during exposure at high temperature. To minimize this attack, the TBC also includes an oxidation-resistant metallic bond coat, which is intended to form a protective alumina scale between the bond coat and the YSZ top coat. Most bond coats are based on a MCrAlY-type (M = Ni and/or Co) composition or Pt aluminides containing high levels of Al that promote the formation of a protective alumina scale without depleting Al in the underlying substrate.

Forming and maintaining this alumina layer (or thermally grown oxide to distinguish it from the deposited top coat oxide) is a major life limiting factor in the performance of TBCs.[4,5,6] Particularly, for the more strain-tolerant electron beam-physical vapor deposited (EB-PVD) coatings, most failures are associated with separation at the metal-alumina interface. If the bond coat cracks or becomes depleted in Al and can no longer form a protective alumina layer, Ni-rich oxide forms at a much faster rate and leads to rapid coating failure.

Given this state-of-the-art, this project examined variations to the general TBC system for both model studies and for alternative applications. A model Ni-base alumina former, β-NiAl + Zr, was used to determine coating performance for an "ideal" alumina former.[7] In this case, ideal means the slowest growing, most adherent alumina scale possible. In addition, oxide-dispersion strengthened (ODS) FeCrAl substrates were coated because of a potential application as the skin of the next generation space shuttle, X-33.[8] This substrate also forms a very adherent alumina scale. Finally, NiCr substrates, which form a chromia scale, were coated to explore the feasibility of a chromia-forming bond coat for applications at lower temperatures (than aero-turbine engines) where hot corrosion may be more of a concern.[9] In general, all of the coatings were successful and showed promise. When failures were observed, they generally followed established failure patterns for commercial coatings.[4,5,6]

2. Experimental Procedure

The substrates in this study included cast NiAl + Zr (0.05 to 0.08 at.% Zr); Y_2O_3-dispersed NiAl; two commercial FeCrAl alloys: Metallwerk Plansee (Lechbruck, Germany) alloy PM2000 (Y_2O_3-dispersed Fe-20 at.% Cr-10Al-0.4Ti) and Kanthal (Hallstahammar, Sweden) alloy APM (ZrO_2-dispersed Fe-20 at.% Cr-10Al-0.4Si); a commercial ODS NiCr alloy: Inco (Huntington, WV) alloy MA758 (Y_2O_3-dispersed Ni-31Cr-0.4Ti); and Y_2O_3-dispersed Ni-27 at.% Cr made by a mechanical alloying process. These alloys are described in detail elsewhere.[7,10–13] They were compared to a commercial EB-PVD YSZ coating on René N5 (PCC, Cleveland, OH) with a Pt aluminide bond coat.[7] All of these alloys contain a reactive element addition (*i.e.,* Y, Zr, or Hf) to improve their oxidation behavior and, in particular, to improve scale adhesion.[12,14–16] Prior to coating, several different surface preparation techniques were used, including a 0.3 μm polish (prior to EB-PVD coating on NiAl) and various grit polishes prior to grit blasting and plasma-sprayed (PS) coating.

B.A. Pint and **I.G. Wright,** Oak Ridge National Laboratory, Oak Ridge, TN 37831-6156; and **W.J. Brindley,** NASA-Lewis Research Center, Cleveland, OH 44135, now with Rolls Royce Allison, Indianapolis, IN 46206-0420.

Coatings were deposited by General Electric Aircraft Engines (Evandale, OH) [125 μm (5 mils) EB-PVD YSZ on NiAl], NASA Lewis Research Center (Cleveland, OH) [125 μm (5 mils) PS YSZ on NiAl, PM2000, APM, and ODS NiCr], and SUNY Stony Brook (Stony Brook, NY) [250 μm (10 mils) PS YSZ on PM2000 and MA758]. In all cases, coupons were coated with YSZ on one side and the edges were relatively sharp and not chamfered. The EB-PVD coatings partially covered the specimen edges with a reduced thickness. The coatings were tested in furnace cycling with dry, flowing oxygen at temperatures from 1000 to 1200 °C. A cycle time of 1 or 2 h indicates time at temperature with typically 10 min cooling between cycles. Samples were removed periodically, visually examined, and weighed on a Mettler Toledo (Hightstown, NJ) model AG245 balance. After oxidation, several samples were sectioned for metallographic analysis to examine the failure mechanism.

3. Results and Discussion

The results and discussion are broken down by substrate type because each represents an application with different objectives.

3.1 NiAl

The primary reason for conducting this experiment was to compare the lifetime of commercial coatings with that of a substrate, which forms an ideal alumina scale.[7] The first set of experiments was performed on EB-PVD-coated, Y_2O_3-dispersed NiAl,[11] which does not form as adherent an alumina scale as does cast NiAl with alloy additions.[10] As a result, failures occurred at relatively short time (Table 1). In each case, analysis of the failed coating revealed fracture at the substrate-alumina interface,[11] which is typical for EB-PVD coatings.[6]

A second set of experiments was performed on NiAl + Zr. In this case, both EB-PVD and PS coatings were tested at 1150 °C (1 h cycles) and 1200 °C (2 h cycles). Figure 1 shows the weight change versus time at 1150 °C. A coated and a similar uncoated substrate were cycled for 4000, 1 h cycles. The uncoated speci-

men showed no weight loss during the test with only minor indications of scale spallation at the edge. Compared to a commercial EB-PVD coating on René N5, which had a lifetime of 650, 1 h cycles, the EB-PVD coating on NiAl + Zr lasted more than 6 times longer without complete failure. As shown in Fig. 2(a) (and corresponding to the weight losses in Fig. 1), there has been extensive chipping near the edge of the sample. A complete loss of the coating represents a weight loss of approximately 30 mg/cm². With a 20% coating loss as the failure criterion, the coating essentially failed at approximately 3800 h. Chipping began at the edges at approximately 1000 h and continued during subsequent cycling. While perfect YSZ adhesion was not observed, the performance was significantly better than that observed for conventional coatings.
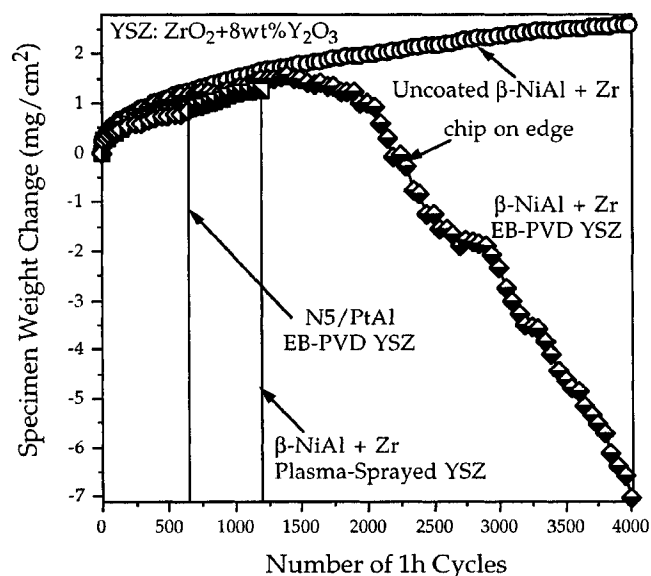

Fig. 1 Specimen weight change during 1 h cycles at 1150 °C of NiAl + Zr with and without a TBC compared to a commercial EB-PVD YSZ coating on René N5 with a Pt aluminide bond coat. The PS coating on NiAl + Zr lasts a factor of 2 longer than the commercial coating on N5. An EB-PVD coating on NiAl + Zr has yet to completely fail after 4000 cycles, but the coating has chipped off the edges

Table 1 Summary of the TBC lifetimes measured in this study in furnace cycles with a dry, flowing O_2 environment

Substrate	1000 °C 1 h cycles	1150 °C 1 h cycles	1200 °C 2 h cycles
René N5 EB-PVD		650	106
NiAl + Y_2O_3 EB-PVD		320	32
NiAl + Zr EB-PVD		≈3800	>740
NiAl + Zr PS		1200	152
ODS FeCrAl PS			290 (average)(a) (200 to 350)
ODS NiCr PS	>1000	450(b)	60(a)

(a) For 1 h cycles at 1200 °C
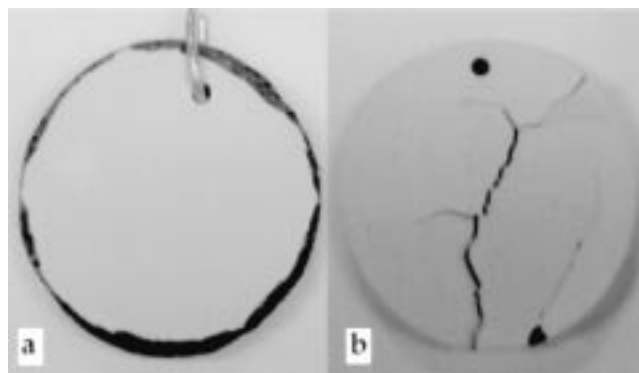(b) For 1 h cycles at 1100 °C

Fig. 2 Photographs of the EB-PVD YSZ coating on (**a**) NiAl + Zr after 3500, 1 h cycles at 1150 °C and (**b**) René N5 + Pt aluminide after 106, 2 h cycles at 1200 °C. In (**a**), the coating has chipped off near the edge but remains largely intact. In (**b**), a massive failure has occurred

At 1200 °C, an improvement in coating lifetime also was observed, with the EB-PVD YSZ coating on NiAl + Zr lasting for more than 740, 2 h cycles with only minimal weight loss (Fig. 3). The EB-PVD coating on René N5 failed after 106 cycles (Fig. 2b). For comparison, the short life (32 cycles) of an EB-PVD YSZ coating on NiAl + Y_2O_3 is also shown in Fig. 3. At 1150 °C, the coating on NiAl + Y_2O_3 also had a shorter lifetime (320 cycles) than the other systems (Table 1).

Results for isothermal oxidation at 1200 °C are shown in Fig. 4. An EB-PVD YSZ coating on one side of NiAl + Zr did not accelerate the alumina growth rate, and the oxide thickness and microstructure were similar to those formed on an uncoated substrate. Also noted in Fig. 4, the scale growth rate of alumina on NiAl + Y_2O_3 is identical to that on NiAl + Zr. The difference between the two alloys is the adhesion of the alumina scale and, in particular, the proclivity for interfacial void formation on NiAl + Y_2O_3.[10]

The PS coating on NiAl + Zr failed after 1200 cycles at 1150 °C, almost a factor of 2 longer than the conventional EB-PVD coating on René N5 but a factor of >3 less than the EB-PVD coating on NiAl + Zr. Similar ratios were also observed at 1200 °C (Table 1). The lower lifetime of the PS coating compared to the EB-PVD coating on NiAl + Zr reflects the greater strain tolerance of the EB-PVD microstructure. After failure of the PS coating at 1200 °C, the specimen was sectioned to observe the failure location (Fig. 5). Typical for PS coatings,[4] more of the alumina scale appears to have remained attached to the NiAl + Zr substrate and a crack has propagated at or near the alumina-YSZ interface. However, with the rougher substrate surface normally used with commercial PS coatings, failure is typically observed in the YSZ with more ceramic remaining attached to the substrate. The slightly rough interface used here was the minimum necessary to deposit a PS coating.[17] Standard practice for PS TBCs would suggest that a rougher substrate/YSZ
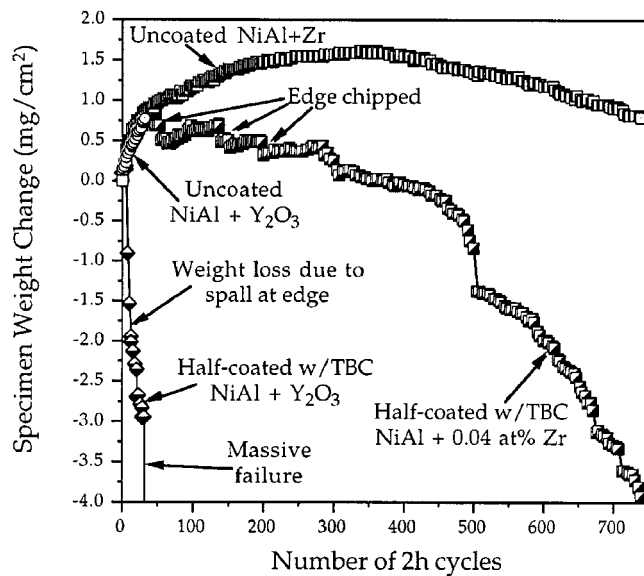
interface would produce a longer lifetime. With the long coating lifetime already demonstrated for the slightly roughened NiAl + Zr substrate, it remains to be seen if the same paradigm holds true for this model system. From the standpoint of alumina scale adhesion, a flatter interface would be preferable to minimize thermal stresses in the scale.[7]
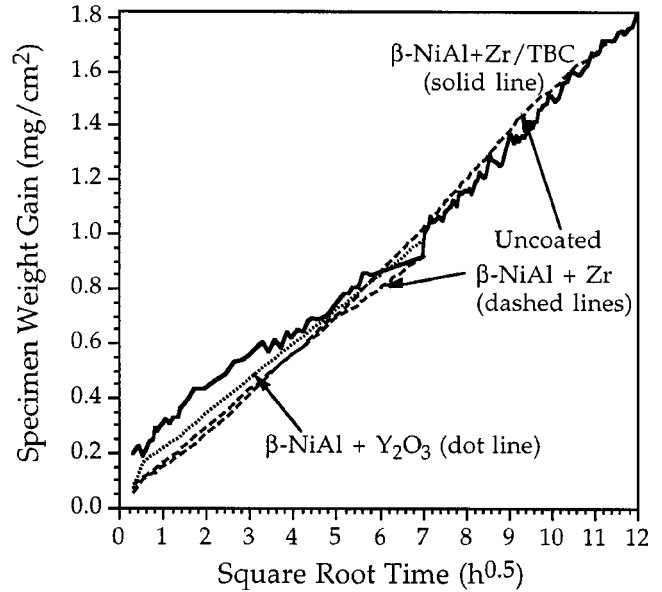

Fig. 4 Specimen weight change during isothermal oxidation at 1200 °C in 1 atm dry flowing oxygen plotted versus the square root of time to show the parabolic relationship. Coating NiAl + Zr on one side with an EB-PVD TBC had no significant effect on the alumina scale growth rate
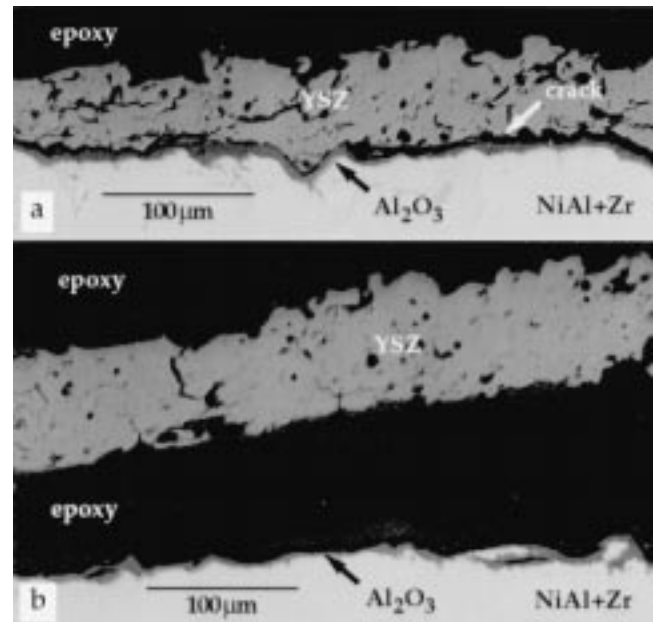

Fig. 3 Specimen weight change during 2 h cycles at 1200 °C of NiAl + Zr and Y_2O_3-dispersed NiAl with and without a 125 mm EB-PVD TBC. NiAl + Zr has lost weight slowly as the edge chipped away. A much more rapid failure occurred for Y_2O_3-dispersed NiAl, because it forms a less adherent alumina scale

Fig. 5 Photographs of a metallographic cross section showing the failure of a PS YSZ coating on NiAl + Zr after 152, 2 h cycles at 1200 °C. In (a) is where the crack begins, while (b) shows where the coating has lifted away from the substrate

3.2 ODS FeCrAl

The design of the next generation space shuttle being developed by Lockheed Martin Corporation, X-33 (Skunk Works, Palmdale, CA) single stage to orbit, reusable launch vehicle, proposes to replace the high maintenance ceramic tiles used on the current space shuttle with a metallic skin.[8] Owing to the volatility of Cr_2O_3, chromia-forming alloys such as NiCr cannot be used for this application.[18] Therefore, the design calls for ODS FeCrAl to achieve the mechanical properties and environmental resistance necessary for a low maintenance protective skin. Since the metallic skin will be limited in thickness, this represents a life-limiting factor for ODS FeCrAl, as there is a limited amount of Al available in the alloy to form and maintain a protective alumina scale.[19] One way to extend the lifetime and operating temperature of the skin is to apply a YSZ layer to ODS FeCrAl, which would reduce the metal temperature during reentry. In order to minimize cost and retain fabrication flexibility on large metal skin panels, the coating would be applied by plasma spraying. While numerous Ni-base alumina formers have been used as bond coat materials, the information available for Fe-base alumina-forming bond coats is mainly for TBCs used at lower temperatures in diesel engines.[20]

In order to test the viability of this concept, PS YSZ was applied to approximately 1 mm thick substrates of PM2000 and APM. Based on the excellent results for PS YSZ coatings on NiAl + Zr and the excellent alumina scale adhesion noted on ODS FeCrAl in general,[11,19,21] testing was conducted at 1200 °C. In this case, the cycle time was 1 h to simulate the short time of reentry. Eight specimens were cycled to failure between 200 and 350 cycles (Fig. 6). A similar weight gain was observed for all of the specimens with and without coatings. In each of the early failure cases, coating spallation did not occur until several days or weeks after removal from the furnace. Because of this association of coating failure with "downtime,"
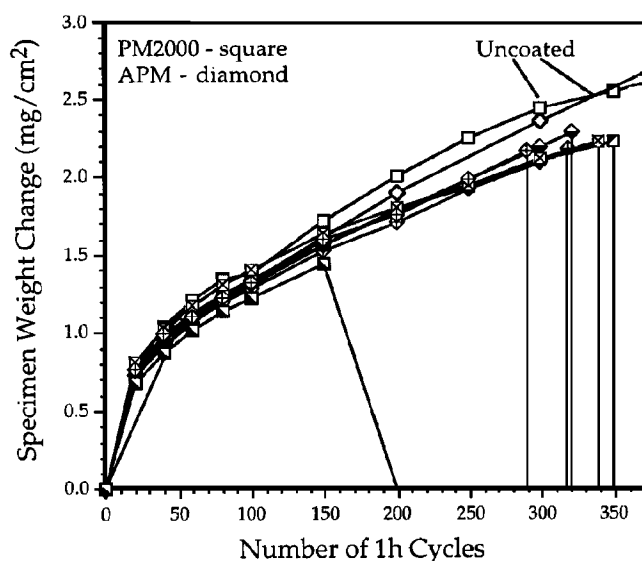
the remaining samples were cycled more slowly after 200 cycles, with only 10 or 20, 1 h cycles per week. Initial surface finishes of as-rolled, 200, 320, and 600 grit were used, but grit blasting the surface prior to YSZ deposition appeared to eliminate any significant effect of this variable. Similar to the observations for NiAl + Zr substrates, these coating lifetimes are significantly higher than conventional PS coatings[4] and are attributed to the excellent alumina scale adhesion on ODS FeCrAl substrates.

The average lifetime of 290 cycles suggests that the concept is viable for the skin of the space shuttle. The coating could be refurbished periodically in the field to prevent failure. However, one area of concern is the observation that some specimens deformed during testing (Fig. 7). Particularly, oxidized coupons of YSZ-coated APM exhibited a convex deformation (with respect to the coated side) due to the presence of the coating (uncoated samples were not observed to deform after 300 cycles). The apparent creep deformation of APM could result from residual stress in the YSZ coating or from the difference in the thermal expansion between coating and substrate. The greater deformation of APM is attributed to its lower strength compared to PM2000. While APM contains a ZrO_2 dispersion, the dispersion is optimized to improve oxidation resistance and not for high-temperature mechanical properties. PM2000 showed much less deformation; however, substrate thicknesses were typically 0.8 to 0.9 mm. A typical metal skin thickness of 0.15 to 0.25 mm (6 to 10 mils) may be more easily deformed by a YSZ coating during high-temperature exposures.

Two of the early failed specimens were sectioned to determine the failure location. Two different modes were observed (Fig. 8). In one case, there appeared to be failure within the alumina scale, with some alumina remaining attached to the substrate and some to the YSZ (Fig. 8a). On the other specimen, a more typical failure in the YSZ near the alumina-YSZ interface was observed (Fig. 8b). On the uncoated side, the alumina scale was adherent and showed no signs of spallation (Fig. 8c). The uncoated interface was less rough than the YSZ-coated side because this side was not grit blasted.
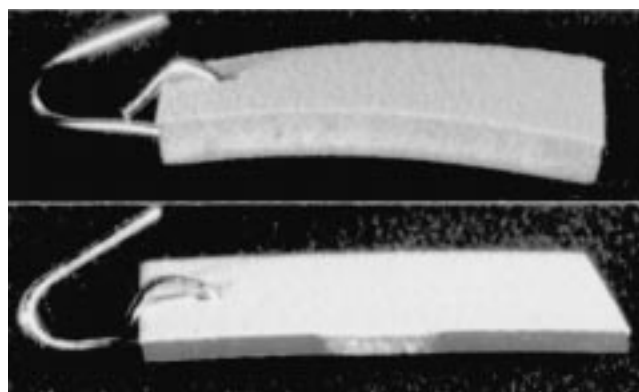

Fig. 6 Specimen weight change at 1200 °C during 1 h cycles of PM2000 (FeCrAl + Y_2O_3) and APM (FeCrAl + ZrO_2) with and without a TBC. Weight gains for all of the specimens were similar. One specimen failed after 200 cycles, but the average lifetime was 290 cycles for eight specimens

Fig. 7 Photographs of (**a**) APM and (**b**) PM2000 after 200, 1 h cycles at 1200 °C (coating on top face only). The APM substrate has deformed during cycling, while the PM2000 substrate is only slightly deflected. The deflection is due to stresses associated with oxidation of the coated specimen; the greater distortion of APM may be due to its lower high-temperature mechanical strength
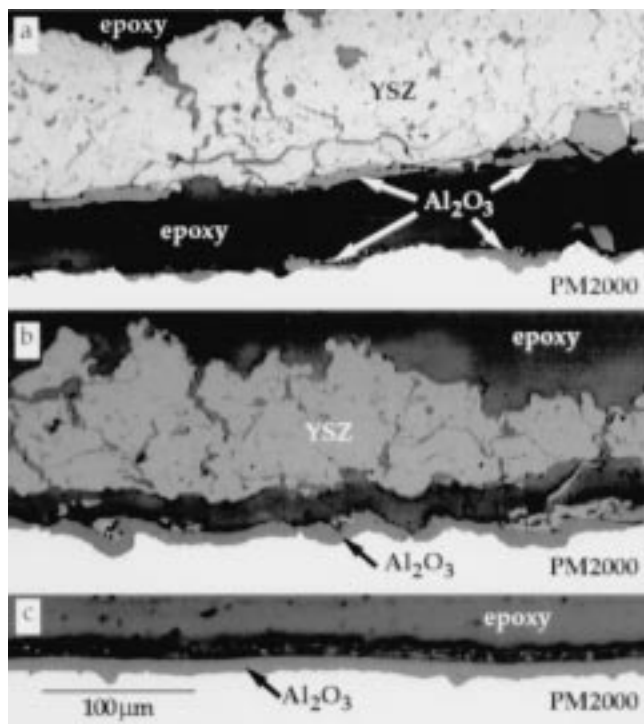
Fig. 8 Photographs of metallographic cross sections showing the PS YSZ coating on PM2000 (FeCrAl + Y_2O_3) after 250, 1 h cycles at 1200 °C. In (**a**), failure occurred within the alumina scale, as scale is attached to both sides of the failure. In a second specimen, (**b**), a more conventional failure was observed in the YSZ near the YSZ-alumina interface. On the uncoated side of the specimen in (**b**), shown in (**c**), the alumina scale is relatively flat and very adherent

3.3 ODS NiCr

These tests were intended as proof of concept experiments to study the feasibility of a chromia-forming bond coat. As with the NiAl work, rather than making a chromia-forming metallic coating, a YSZ layer was applied to NiCr substrates in order to simplify the experiment. NiCr with a Y_2O_3 dispersion was chosen because it is known to form a very adherent and slow-growing chromia scale as a result of the beneficial effect of Y.[14–16,22,23] Alloy chromium contents were above 25 at.% to limit the formation of a $NiCr_2O_4$ transient oxide layer.

These chromia-based bond coats are intended to be used at lower temperatures; therefore, these specimens were cycled primarily at 1000 °C. None of the coatings failed during 1000, 1 h cycles. Three different types of substrates were coated: MA758 (Ni-31Cr + Y_2O_3), Ni-27Cr + 0.2Y (as Y_2O_3), and Ni-27Cr + 0.3Y (as Y_2O_3). The Ni-27Cr alloys had more porosity than MA758 with Ni-27Cr-0.2Y containing the most. As a result of this porosity in Ni-27Cr-0.2Y, the alloy had a higher weight gain due to a higher effective surface area (Fig. 9). However, the other two alloys had similar weight gains. An uncoated substrate was also included in the test. The weight losses observed are due to volatilization of CrO_3,[22] and, with similar weight losses for the coated and uncoated specimens (Fig. 9), it appears that the YSZ coating does not inhibit this volatilization. One specimen of Ni-27Cr-0.3Y was stopped after 250 cycles for sectioning (Fig. 10). With light microscopy,
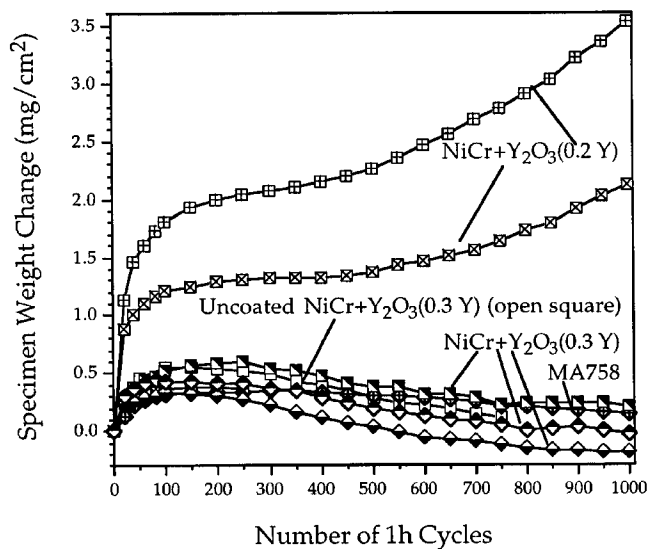

Fig. 9 Specimen weight change during 1 h cycles at 1000 °C of Y_2O_3-dispersed NiCr with and without a TBC. Weight gains are higher for one version of Ni-25Cr with 0.2Y because of a greater amount of alloy porosity. None of the coatings failed during this exposure
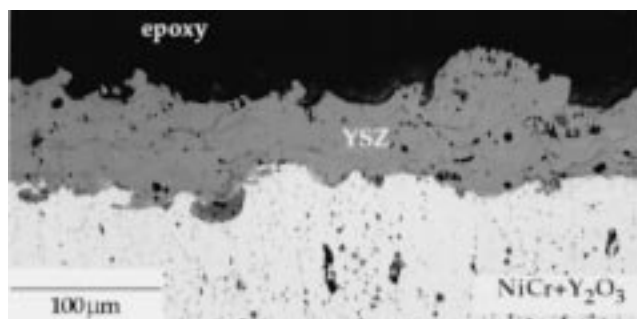

Fig. 10 Photograph of a metallographic cross section showing the PS YSZ coating on NiCr + Y_2O_3 (0.3Y) after 250, 1 h cycles at 1000 °C. In this image, no clear chromia scale is identified and no failure has been observed

no clear chromia layer was observed, which is unusual since the alumina layer is clearly visible in Fig. 5 and 8. Future characterization work will attempt to identify a reaction product. The cross section revealed the large amount of porosity and oxide particles in the alloy.

In order to induce coating failure, MA758 coupons were given 1 h cycles at 1100 and 1200 °C. The coating delaminated after 450, 1 h cycles at 1100 °C. At 1200 °C, one coupon failed after 60 cycles with the YSZ coating completely delaminating (Table 1). A second specimen was cycled for 20, 1 h cycles and then sectioned (Fig. 11). Again, no obvious chromia scale was observed. In this case, cracking can be seen near the substrate-YSZ interface, indicating that failure was imminent. The failed specimen appeared to fail at or near the substrate-YSZ interface.

In these initial experiments, there appears to be some promise for an acceptable chromia-forming bond coat with a YSZ top coat. However, further testing will be required to verify this result. Of particular interest is the detection of the Cr_2O_3 reaction product to determine its effect on coating lifetime.
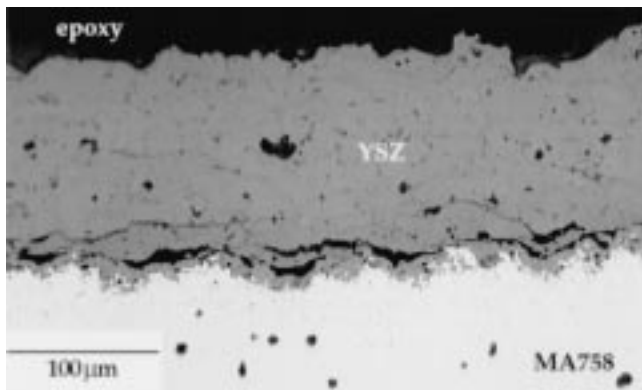
Fig. 11 Photograph of a metallographic cross section showing the PS YSZ coating on MA758 (NiCr + Y_2O_3) after 20, 1 h cycles at 1200 °C. No clear chromia layer can be identified. Extensive cracking has occurred in the YSZ layer near the metal

4. Summary and Conclusions

Several different oxidation-resistant substrates were investigated to determine the cyclic lifetimes of a YSZ top coat at high temperature. For NiAl, the testing revealed that a more adherent alumina scale may extend the lifetime of commercial EB-PVD and PS coatings. A YSZ coating on an ODS FeCrAl alloy holds particular promise for the metallic skin of the next generation space shuttle. One area of concern is the possibility that a thin metal substrate will be deformed by coating-induced creep deformation. Future work should focus on a thin section ODS FeCrAl substrate to further investigate this aspect of the proposed coating. Finally, in initial testing, a chromia-forming substrate appeared to support a YSZ coating. This type of bond coat may be promising for lower temperature, corrosive environments or in cases where the substrate contains little or no Al. In each case, the YSZ coating did not appear to affect the rate of alumina or chromia scale formation beneath the coating. In general, this work has extended the basic premise for using TBCs to other material systems, but the same fundamental life-limiting factors and mechanisms found in conventional TBC systems also appear to be relevant in these novel systems.

Acknowledgments

References

1. R.A. Miller: *J. Am. Ceram. Soc.,* 1984, vol. 67, pp. 517-21.
2. A. Bennett: *Mater. Sci. Technol.,* 1986, vol. 2, pp. 257-61.
3. T.A. Cruse, S.E. Stewart, and M. Ortiz: *J. Eng. Gas Turb. Power,* 1988, vol. 110, pp. 610-16.
4. R.A. Miller: *J. Eng. Gas Turb. Power,* 1989, vol. 111, pp. 301-05.
5. J.T. DeMasi-Marcin, K.D. Sheffler, and S. Bose: *J. Eng. Gas Turb. Power,* 1990, vol. 112, pp. 522-27.
6. S.M. Meier, D.M. Nissley, K.D. Sheffler, and T.A. Cruse: *J. Eng. Gas Turb. Power,* 1992, vol. 114, pp. 258-63.
7. B.A. Pint, I.G. Wright, W.Y. Lee, Y. Zhang, K. Prüßner, and K.B. Alexander: *Mater. Sci. Eng.,* 1998, vol. A245, pp. 201-11.
8. B. Strauss and J. Hulewicz: *Adv. Mater. Process,* 1997, vol. 151 (5), pp. 55-56.
9. R.A. Rapp: *Corrosion,* 1986, vol. 42, pp. 568-77.
10. B.A. Pint: *Oxid. Met.,* 1998, vol. 49, pp. 531-60.
11. B.A. Pint: *Mater. High Temp.,* 1997, vol. 14, pp. 403-12.
12. B.A. Pint, A.J. Garratt-Reed, and L.W. Hobbs: *Mater. High Temp.,* 1995, vol. 13, pp. 3-16.
13. B.A. Pint, C. Roberts, and I.G. Wright: *Oxid. Met.,* submitted for publication.
14. D.P. Moon: *Mater. Sci. Technol.,* 1989, vol. 5, pp. 754-64.
15. A. Strawbridge and P.Y. Hou: *Mater. High Temp.,* 1994, vol. 12, pp. 177-81.
16. B.A. Pint: *Oxid. Met.,* 1996, vol. 45, pp. 1-37.
17. R.A. Miller and W.J. Brindley: in *Thermal Spray: International Advances in Coatings Technology,* C.C. Berndt, ed., ASM International, Materials Park, OH, 1992, pp. 493-98.
18. M.A. Gedwill and S.J. Grisaffe: "Evaluation of NiCrAl and FeCrAlY Claddings on TD-NiCr: Mach 1 Burner Rig Tests at 2100 °F (1149 °C)," NASA TM X-52916, NASA Lewis Research Center, Cleveland, OH, 1970.
19. W.J. Quadakkers and M.J. Bennett: *Mater. Sci. Technol.,* 1994, vol. 10, pp. 126-31.
20. D. Zhu and R.A. Miller: in *Fundamental Aspects of High Temperature Corrosion,* D.A. Shores, R.A. Rapp, and P.Y. Hou, eds., Electrochemical Society, Pennington, NJ, 1996, vol. PV96-26, pp. 289-307.
21. B.A. Pint, P.F. Tortorelli, and I.G. Wright: *Mater. High Temp.,* 1999, vol. 16, pp. 1–13.
22. J. Stringer, B.A. Wilcox, and R.I. Jaffee: *Oxid. Met.,* 1972, vol. 5, pp. 11-47.
23. K. Przybylski and G.J. Yurek: *Mater. Sci. Forum,* 1989, vol. 43, pp. 1-74.